Comparison of electrochemical behavior of exohedral palladium complexes with [60]- and [70]-fullerenes and metallocene ligands

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Electronic structures of exohedral palladium complexes of [60]- and [70]-fullerenes with diphenylphosphinoferrocenyl, diphenylphosphinoruthenocenyl, and diphenylphosphinocymantrenyl ligands were studied by cyclic voltammetry and semiempirical quantum-chemical calculations. Probable sites of localization of electronic changes in the molecules of these complexes under electrochemical oxidation and reduction were determined.

Key words: fullerenes, exohedral palladium complexes, cymantrene, ruthenocene, electronic structure, voltammetry, semiempirical calculations.

We have recently[1,2] synthesized a series of new exohedral Pd^0 complexes with [60]- and [70]-fullerenes containing 1,1´-bisdiphenylphosphinoferrocene (dppf), 1,1´-bisdiphenylphosphinoruthenocene (dppr), or two diphenylphosphinocymantrene (dppcym) molecules as stabilizing ligands. These complexes contain a strongly electron-withdrawing fullerene cage and a metallocene group, which can be either electron-releasing (ruthenocene) or electron-withdrawing (cymantrene) and is linked with the cage through the bisdiphenylphosphinepalladium bridge. Intramolecular charge transfer can occur between these groups and the fullerene core and should affect the electrochemical reduction potentials (E^{Red}) of the fullerene moiety (C_{60}, C_{70}), which is active in the cathodic potential region, and oxidation potentials (E^{Ox}) of the metallocene group, which is active in the anodic region. The electrochemical pattern is impeded by the fact that the bisdiphenylphosphinepalladium fragment linking these terminal groups is also redox-active.

In this work, we studied and compared the C_{60}Pd(dppf), C_{60}Pd(dppr), C_{60}Pd(dppcym)$_2$, C_{70}Pd(dppr), and C_{70}Pd(dppcym)$_2$ complexes by cyclic voltammetry (CV) and semiempirical quantum-chemical calculations using available X-ray diffraction data to elucidate the electronic structures of these complexes and to reveal redox sites (*i.e.*, sites of localization of electronic changes) responsible for the electrochemical reduction and oxidation. The data obtained can be helpful for evaluation of these compounds to be used as electro- and photoactive materials, catalysts, *etc.*

Experimental

The C_{60}Pd(dppf), C_{60}Pd(dppcym), C_{60}Pd(dppr), C_{70}Pd(dppcym), and C_{70}Pd(dppf) complexes were synthesized using a Schlenk technique by a previously described method.[1,2] The latter includes the reaction of equivalent amounts of the respective fullerene, $Pd_2(dba)_3$ complex (dba is dibenzylideneacetone), and phosphine ligand under argon.

Measurements of E^{Ox} and E^{Red} were carried out using a digital IPC Win potentiostat-galvanostat. Voltammograms were recorded with 0.15 *M* $Bu^n{}_4NBF_4$ as a supporting electrolyte in *o*-dichlorobenzene at 20 °C in a 10-mL electrochemical cell. Oxygen was removed with dry argon passed through the cell. The CV curves were recorded on a stationary graphite electrode with a sweep rate of 100 and 200 mV s^{-1}. Potentials of peaks, which were often poorly pronounced in CV curves, were determined by a special program installed in the IPC Win program package. Measured values were recalculated taking into account ohmic losses.

Pyrolyzed polyacrylonitrile (PAN) with a specific surface of 12 m^2 g^{-1} was used as the material for a working electrode. An auxiliary electrode was platinum, and a saturated Ag/AgCl electrode was a reference electrode.

Calculations were performed by the ZINDO/1 method included in the HyperChem program package.

o-Dichlorobenzene (reagent grade) was purified with calcium hydride for 4 h and distilled *in vacuo* collecting a fraction with b.p. 48 °C (10 Torr). Prior to use, the supporting electrolyte $Bu^n{}_4NBF_4$ was twice recrystallized from anhydrous toluene and dried.

Qualitative measurements of absorbance in the electronic spectra (Specord UV—Vis) for a solution of C_{60}Pd(dppcym)$_2$

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were carried out in an open cell with periodical sampling of the solution, which contacted with air.

Results and Discussion

All complexes under study are scarcely soluble in the most part of solvents. Therefore, only *o*-dichlorobenzene (DCB) and a toluene—MeCN (4 : 1, vol/vol) mixture turned out to be appropriate for electrochemical studies; however, even in this case, the concentration of the complexes did not exceed $1 \cdot 10^{-4}$ mol L^{-1}. Moreover, the complexes are unstable in solutions. The cymantrene complexes, whose solutions contain a mixture of products including free fullerenes, are especially unstable. The dynamics of changing the electronic spectrum of C_{60}Pd(dppcym)$_2$ in toluene in the presence of oxygen traces is presented in Fig. 1. The intensity of the characteristic absorption bands of C_{60}Pd(dppcym)$_2$ at 22780, 16260, and 15260 cm^{-1} decreases sharply, which indicates that the compound is unstable under these conditions. Fullerene is a product of C_{60}Pd(dppcym)$_2$ decomposition. The other products of decomposition of C_{60}Pd(dppcym)$_2$ in air were not studied in this work.

Using PAN as a working electrode, one can obtain more pronounced peaks of redox transitions than those, *e.g.*, when smooth Pt is used.

The voltammograms for the exohedral palladium complexes of C_{60} with the ferrocenyl-, ruthenocenyl-, and cymantrenyl-containing phosphine ligands are presented in Fig. 2.

The CV curves of the complexes are similar. The shape of the curves is complicated because the molecules contain three redox-active sites. In addition, a possible partial dissociation of the complexes in solutions and their oxidation with oxygen traces often produce many peaks in the CV curves, especially in the cathodic region, due to which their interpretation is often difficult.

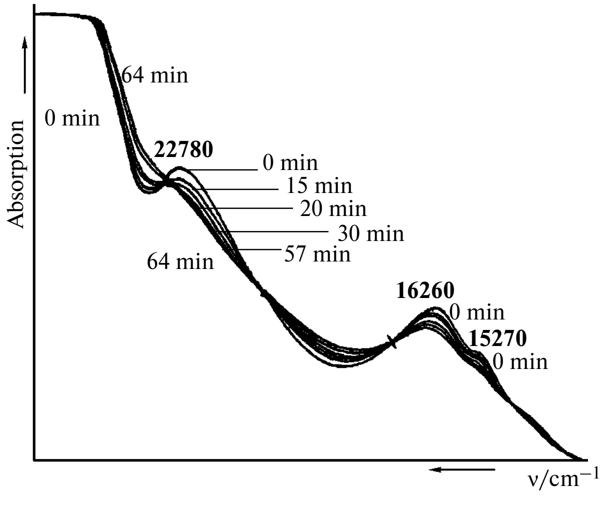


Fig. 1. Time changes in the electronic absorption spectrum of C_{60}Pd(dppcym)$_2$ in the presence of oxygen traces in a toluene solution.

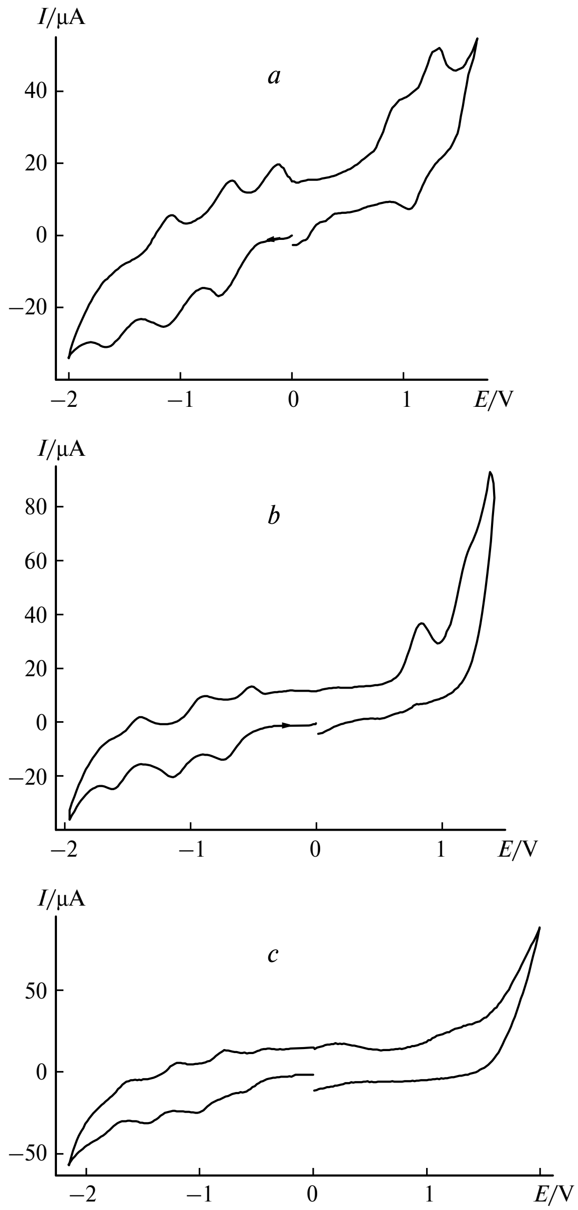


Fig. 2. Voltammograms of the heterobimetallic complexes of C_{60}: C_{60}Pd(dppf) (*a*), C_{60}Pd(dppr) (*b*), and C_{60}Pd(dpcym)$_2$ (*c*) (PAN, *o*-dichlorobenzene, 0.15 *M* Bu_4NBF_4, *vs.* Ag/AgCl/KCl, 200 mV s^{-1}).

The reduction potentials of C_{60}Pd(dppcym)$_2$ and C_{70}Pd(dppcym)$_2$, which were measured by us earlier[3] and virtually coincided with the reduction potentials of free C_{60} and C_{70}, are incorrect, probably, because of partial destruction of the complexes. The data given in Table 1 are correct. In special experiments, we succeeded to obtain (on PAN) well discernible reduction peaks for a mixture of C_{60}Pd(dppcym)$_2$ and C_{60} in a ratio of 1 : 2 (Fig. 3). The use of vacuum in preparing solutions of

Table 1. Oxidation (E^{Ox}) and reduction (E^{Red}) potentials of the C_nML_2 complexes (M = Pd, Pt; L_2 = dppf, dppr, $(dppcym)_2$; n = 60, 70) and free fullerenes*

Compound	E^{Ox}	$-E^{Red}$
	V	
η^2-C_{60}Pd(dppf)	0.87, 1.22	0.69, 1.04, 1.52
η^2-C_{60}Pd(dppr)	0.82, 1.16	0.61, 0.96, 1.34
η^2-$C_{60}Pd(dppcym)_2$	1.03, 1.44	0.60, 0.97, 1.38
η^2-C_{70}Pd(dppr)	0.86, 1.20	0.63, 0.98, 1.40
η^2-$C_{70}Pd(dppcym)_2$	1.03, 1.35	0.61, 0.99, 1.41
C_{60}	—	0.41, 0.78, 1.20
C_{70}	—	0.41, 0.77, 1.19

* Experimental conditions: DCB, PAN electrode, 0.15 *M* Bu_4NBF_4, *vs.* Ag/AgCl/KCl.

$C_{60}Pd(dppcym)_2$ and $C_{70}Pd(dppcym)_2$ also made it possible to detect pronounced reduction peaks of the individual complexes in the voltammograms (see Fig. 2).

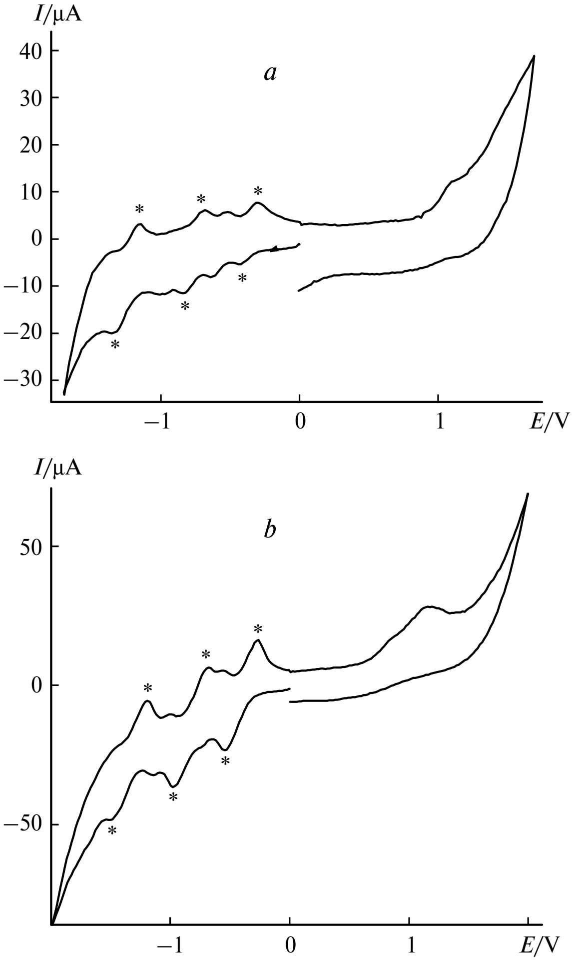


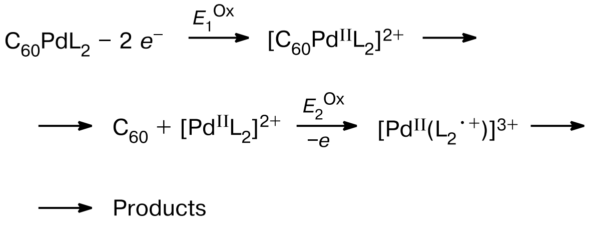
Fig. 3. Voltammograms of the $C_{60}Pd(dppcym)_2$—C_{60} (*a*) and C_{60}Pd(dppr)—C_{60} (*b*) mixtures in *o*-dichlorobenzene (PAN, 0.15 *M* Bu_4NBF_4, *vs.* Ag/AgCl/KCl, 200 mV s^{-1}). Peaks of C_{60} are marked by asterisks.

For all complexes, the E^{Red} values are shifted to the cathodic region compared to E^{Red} of free fullerenes (see Fig. 3), which can be interpreted as a consequence of charge transfer from the metal-containing fragment to the fullerene moiety of the molecule.

The first peak in the voltammograms in the anodic region for all complexes is irreversible and corresponds to two-electron oxidation. The E^{Ox} values of this redox transition lie within the interval from 0.85 to 1.05 V (*vs.* Ag/AgCl/KCl), depending on the nature of the metallocenylphosphine ligand. In the case of C_{60}Pd(dppf) and C_{60}Pd(dppr), the second anodic peak is observed at potentials close to the oxidation potentials of the respective 1,1′-metallocenyl(bisdiphenylphosphinepalladium) dichlorides (*e.g.*, 1.22 V for C_{60}Pd(dppf) and 1.20 V for $Pd(dppf)Cl_2$).

Based on the CV data, we can propose the following sequence of the initial steps of electrochemical oxidation of C_{60}Pd(dppf) and C_{60}Pd(dppr) (Scheme 1).

Scheme 1



$$C_{60}PdL_2 - 2\,e^- \xrightarrow{E_1^{Ox}} [C_{60}Pd^{II}L_2]^{2+} \longrightarrow$$

$$\longrightarrow C_{60} + [Pd^{II}L_2]^{2+} \xrightarrow[-e]{E_2^{Ox}} [Pd^{II}(L_2^{\cdot +})]^{3+} \longrightarrow$$

$$\longrightarrow \text{Products}$$

It is likely that the two-electron oxidation of the complex at E_1^{Ox} mainly concerns Pd, and the dication formed dissociates rapidly to free fullerene and $[Pd^{II}L_2]^{2+}$ dication, which is probably coordinated with the solvent molecules. The latter peak at E_2^{Ox} is attributed to the oxidation of the metallocene moiety of the complex.

To verify the above assumptions on localization of the redox-active sites in the complexes, we performed semiempirical calculations of frontier orbital energies by the ZINDO/1 method[4,5] included in the HyperChem program package (HyperCube Inc., FL, USA). The geometry of molecules was optimized by the ZINDO/1 method for singlet states using a restricted Hartree—Fock theory. Geometry optimization was performed with the fixed convergence gradient at most 10 cal $Å^{-1}$ mol^{-1}. In the HyperChem program, parameters were used by default.

The semiempirical calculations showed that the lowest unoccupied molecular orbital (LUMO) for the $C_{60}PdL_2$ complexes (L_2 = dppf, dppr, $(dppcym)_2$) is localized on the fullerene cage, and the metal-containing fragment makes virtually no contribution to this orbital (Fig. 4). For the complexes with L_2 = dppf and dppr, the main contribution to the formation of the highest occupied

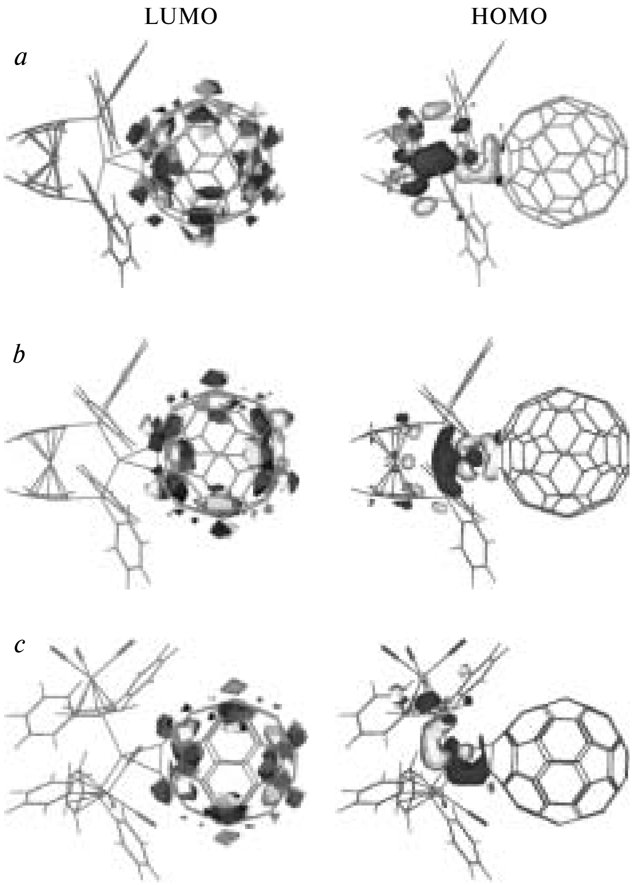


Fig. 4. LUMO and HOMO calculated for $C_{60}Pd(dppf)$ (*a*), $C_{60}Pd(dppr)$ (*b*), and $C_{60}Pd(dppcym)_2$ (*c*).

Table 2. Lengths (*d*) of the shortest C—C bond in fullerenes C_{60} and C_{70} and the C—C metal-coordinating bond in C_nML_2

Compound	d/Å	Ref.
$C_{60}Pt(PPh_3)_2$	1.502(30)	7
$C_{60}Pd(PPh_3)_2$	1.447(25)	8
$C_{60}Pd(dppcym)_2$	1.472(7)	2, this work
$C_{60}Pd(dppr)$	1.476(9)	2, this work
$C_{70}Pd(dppr)$	1.476(9)	2, this work
C_{60}	1.39	9
C_{70}	1.380	10

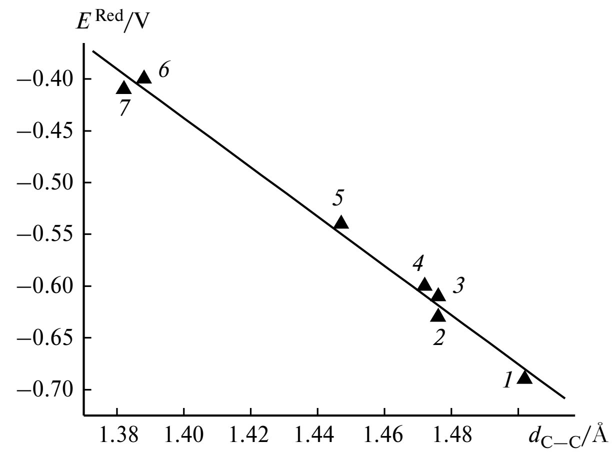


Fig. 5. Relationship between the C(1)—C(2) bond length (d_{C-C}) and the reduction potential (E^{Red}) of the η^2-fullerene complexes: $C_{60}Pt(PPh_3)_2$ (*1*), $C_{60}Pd(dppcym)_2$ (*2*), $C_{60}Pd(dppr)$ (*3*), $C_{70}Pd(dppr)$ (*4*), $C_{60}Pd(PPh_3)_2$ (*5*), C_{60} (*6*), and C_{70} (*7*).

molecular orbital (HOMO) is made by the orbitals of Pd involving the ferrocene or ruthenocene fragment. In the case of the cymantrenylpalladium complex, the HOMO is distributed over the P—Pd—P fragment involving no cymantrenyl groups (unlike two preceding complexes). Thus, the electrochemical potentials and results of calculations agree. Therefore, one can conclude that reduction primarily involves the fullerene orbitals, whereas oxidation involves the orbitals of palladium.

The X-ray diffraction data on the complexes* showed that the Pd atom coordinated with the double bond of fullerene and two P atoms has the planar configuration, which agrees with the published data**6** for other similar complexes. The C—C bond in the palladocycle elongates considerably upon coordination compared to that in free fullerene (Table 2), and the degree of pyramidality of the C atoms bound to Pd also changes.

The elongation of the C—C bond in the metal-coordinated fullerene over that in free fullerene affects substantially the reduction potentials of the complexes. The exohedral fullerene complexes exhibit an interesting relationship between the electrochemical and X-ray diffraction data. It is more difficult to reduce the exohedral fullerene complex with a longer C—C bond (Fig. 5). In other words, the stronger an extension of the C=C bond of the fullerene cage upon coordination, the higher an increase in the LUMO energy and the more difficult the reduction of the complex. The correlation shown in Fig. 5 ($r = 0.996$) is described by a linear equation

$$E^{Red} = -2.37d_{C-C} + 2.88,$$

i.e., the potential values are rather sensitive to a change in the geometry (correlation coefficient 2.37 V Å^{-1}).

The correlation of E_1^{Red} with the geometry of the complexes shows the sensitivity of the electron affinity of the fullerene cage to the distortion of its geometry: ideal structures with the symmetry I_h (C_{60}) and D_{5h} (C_{70}) have the highest electron affinity, and any deviations from the perfect geometry decrease the withdrawing properties of the core.

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* Complete X-ray diffraction data for the $C_{60}Pd(dppcym)_2$, $C_{60}Pd(dppr)$, and $C_{70}Pd(dppr)$ complexes will be published elsewhere.

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