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Metallation of fullerenes: electrochemical synthesis and voltammetric study of heterometallic C_{60} and C_{70} complexes

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Electrochemical synthesis and voltammetric study of new heterotrimetallic exohedral derivatives of [60]- and [70]fullerenes containing palladium and manganese atoms were carried out. The MO involved in redox transitions were determined by the semiempirical quantum-chemical calculations and by the comparison of the potentials for the redox transitions of the heterotrimetallic complexes and their fullerene and metal-containing fragments.

Key words: fullerenes, metallation, Platinum Group metal complexes, electrosynthesis, voltammetry, semiempirical calculations.

Interest in the chemistry of organometallic fullerene derivatives was provoked by the combination in the same molecule of the fullerene cage, which is electroactive in the cathodic potential region,[1—3] and organometallic fragment, which can undergo redox transitions in the anodic region. This combination allows the use of such compounds as catalysts, materials for non-linear optics, sensors, *etc*.[4,5] The study of charge transfer processes in such systems is of independent theoretical significance.

Application of electrochemical methods provides great challenges in the organometallic chemistry of fullerenes due to the combination of their analytical and preparative potentialities. We have previously[6,7] proposed a method for synthesis of the exohedral metal complexes of [60]fullerenes $C_{60}ML_2$ (M = Pd, Pt; $L_2 = (PPh_3)_2$, dppf (bis(diphenylphosphino)ferrocene)). Organometallic fullerene derivatives containing two and more metal atoms in the molecule are of special interest. We have recently[7] synthesized the bimetallic complex of [60]fullerene containing the dppf-palladium fragment and studied its electrochemical and spectral properties. Exploring this approach further in this work, we electrochemically synthesized and studied the electronic structure of the new heterotrimetallic complexes of [60]- and [70]fullerenes with the cymanthrenyldiphenylphosphine ligands.

Experimental

Instruments and electrodes. Electrochemical oxidation and reduction potentials were measured using an IPC-Win potentiostate-galvanometer connected with a personal computer. Measurements were performed at 20 °C using a stationary Pt electrode with a working surface of 5.14 mm^2 or a graphite electrode from pyrolyzed polyacrylonitrile* in anhydrous *o*-dichlorobenzene with 0.15 *M* $Bu^n{}_4NBF_4$ as supporting electrolyte. The concentration of the compounds in solutions was $(1—3) \cdot 10^{-4}$ mol L^{-1}.

The scan rate in cyclic voltammetry (CV) was 200 mV s^{-1}. The platinum electrode was thoroughly polished with a diamond paste after recording each curve. The fullerene anions were generated using a P-5827M potentiostate in a two-compartment electrolytic cell on a Pt electrode (plate with a surface area of 2.29 cm^2) with $Bu^n{}_4NBF_4$ as a supporting electrolyte in anhydrous *o*-dichlorobenzene at 20 °C.

In all cases, Pt served as the auxiliary electrode, and a saturated silver-chloride electrode was a reference electrode.

Purification of solvents and supporting electrolyte. *o*-Dichlorobenzene (high-purity grade) was stirred above CaH_2 for 1 h with heating and distilled *in vacuo*, and the fraction with b.p. 48 °C (10 Торр) was collected. $Bu^n{}_4NBF_4$ was doubly recrystallized from anhydrous toluene and dried.

Synthesis of initial compounds. All reactions were carried out under argon using the Schlenk technique. The η^2-$C_{60}Pd[Ph_2P$-η^5-C_5H_4-$Mn(CO)_3]_2$ (**1**)** and η^2-$C_{70}Pd[Ph_2P$-η^5-C_5H_4-$Mn(CO)_3]_2$ (**2**) complexes were prepared by the reaction of equivalent amounts of the corresponding fullerene, $Pd_2(dba)_3$ complex (dba is dibenzylideneacetone), and the ligand (diphenylcymanthrenylphosphine) using a previously published

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* Hereafter "graphite electrode" designates the graphite electrode from pyrolized polyacrylonitrile.

** Found (%): C, 75.77; H, 2.07; P, 3.48. $C_{100}H_{28}Mn_2O_6P_2Pd \cdot C_6H_6$. Calculated (%): C, 75.71; H, 2.04; P, 3.68.

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procedure.[8] The Ph_2P-η^5-C_5H_4-$Mn(CO)_3$ complex was synthesized[9] by the metallation of cymanthrene with BuLi followed by the addition of Ph_2PCl.

Reactions of the C_{60}^{2-} and C_{70}^{2-} dianions with $PdCl_2$ in the presence of the cymanthrenylphosphine ligand. Fullerene C_{60} (0.0015 g, $2.1 \cdot 10^{-6}$ mol) was dissolved in *o*-dichlorobenzene (7 mL) containing $Bu^n{}_4NBF_4$ (0.15 mol L^{-1}). Preparative electrolysis was carried out at –0.9 V for 2 h. Dry argon saturated with the solvent vapor was passed through a solution of the electrolyte to remove O_2 and stirring the solution. The electrolysis course was monitored by a change in the electrolysis current until the residual current became less than 10—15% of the initial value. A dark red solution of the C_{60}^{2-} dianion was introduced into a Schlenk tube containing 2 mL of a suspension of $PdCl_2$ (0.0004 g, $2.2 \cdot 10^{-6}$ mol) and cymanthrenylphosphine (0.0017 g, $4.4 \cdot 10^{-6}$ mol) in *o*-dichlorobenzene. Argon was bubbled through this mixture. After addition of C_{60}^{2-}, $PdCl_2$ was dissolved, and the solution slowly (for ~2 h) gained a green color characteristic of monometallic fullerene C_{60} derivatives.

The C_{70}^{2-} dianion was generated analogously. The resulting solution of the dianion was conveyed into a Schlenk tube containing a suspension of $PdCl_2$ and cymanthrenylphosphine in *o*-dichlorobenzene. After this $PdCl_2$ dissolved, and the solution became reddish-brown, which is characteristic of the monometallic fullerene C_{70} derivatives.

Complexes **1** and **2** were identified electrochemically by comparison of the potentials of the redox transition peaks with those for the authentic sample.

Results and Discussion

Fullerenes C_{60} and stable ML_2Cl_2 complexes or MCl_2 salts (M = Pd, Pt; L_2 = $(PPh_3)_2$, dppf) containing the metal atom in the oxidation state +2 were used as initial compounds in our earlier[6,7] method proposed for electrochemical synthesis of the exohedral metal complexes of [60]fullerenes $C_{60}ML_2$.

Two-electron electrochemical reduction of fullerene affords the corresponding dianion. The latter, being added to ML_2Cl_2, irreversibly reduces the M^{II} complex and transforms into a neutral molecule. Thus formed two neutral molecules (C_n and ML_2) further react with each other:

$$C_n + 2\,e \rightleftharpoons C_n^{2-},$$

$$C_n^{2-} + ML_2Cl_2 \longrightarrow C_n + ML_2 + 2\,Cl^-,$$

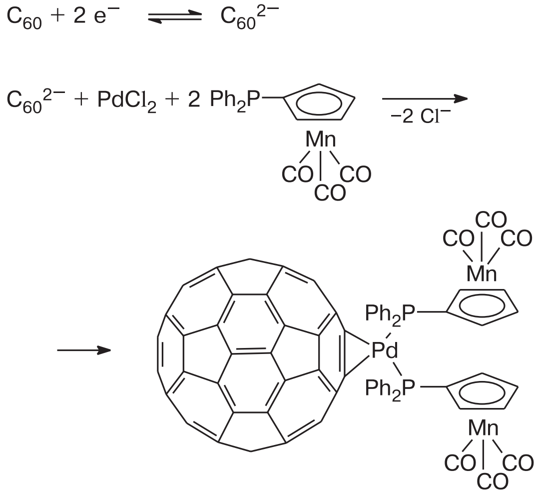
$$C_n + ML_2 \longrightarrow C_nML_2,$$

$n = 60, 70.$

In this case, the C_n molecule acts simultaneously as a mediator and one of the structure-forming reactants. All advantages of mediatory chemical reactions, *viz*., low overpotential, high selectivity, and high yield, are manifested in this process. Therefore, it is not necessary to introduce an additional redox pair into the system.

In this work, this approach was extended to the synthesis of new heterotrimetallic [60]- and [70]fullerene complexes with the cymanthrenyldiphenylphosphine ligands (see Scheme 1 for fullerene C_{60}).

Scheme 1



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The electrochemical properties of all reactants and target products were studied before the beginning of the electrochemical synthesis of complexes **1** and **2**. With this purpose, complexes **1** and **2** were synthesized[8] chemically from the Pd^0 complexes with dba.

$$Pd_2(dba)_3 \cdot C_6H_6 + 4\,CymPPh_2 + 2\,C_n \longrightarrow$$

$$\longrightarrow \underset{\mathbf{1},\,\mathbf{2}}{2\,C_nPd(CymPPh_2)_2} + 3\,dba + C_6H_6,$$

Cym — $(C_5H_4)Mn(CO)_3$, n = 60 (**1**), 70 (**2**).

[60]- and [70]Fullerenes. The electrochemical properties of [60]- and [70]fullerenes have been studied in detail.[1—3] They are characterized by six reversible redox transitions in the cathodic potential region (0 to –2.5 V *vs*. Ag/AgCl/KCl); no redox transition is observed in the anodic potential region (0—1.5 V *vs*. Ag/AgCl/KCl).[2,3,10,11] The potentials measured by us on a special graphite electrode (*o*-dichlorobenzene, 0.15 *M* $Bu^n{}_4NBF_4$, Ag/AgCl/KCl) are presented in Table 1.

Bis(diphenylcymanthrenylphosphine)palladium chloride. This complex was synthesized by the reaction

$$PdCl_2 + 2\,CymPPh_2 \longrightarrow (CymPPh_2)_2PdCl_2,$$

whose course can be monitored by CV from the appearance of a new cathodic peak at E = –1.06 V (Fig. 1). This value is close to the potential of Pd reduction in $(Ph_3P)_2PdCl_2$.[12] Therefore, the peak with E = –1.06 V can be assigned to the reduction process

$$Pd^{II} + 2\,e \longrightarrow Pd^0.$$

Table 1. Potentials of the oxidation ($E^{\rm Ox}$) and reduction ($E^{\rm Red}$) peaks in the CV curves for the initial compounds, reaction mixtures, and target products (graphite electrode, *o*-dichlorobenzene, 0.15 *M* $Bu^n{}_4NBF_4$, Ag/AgCl/KCl)

Compound or mixture	$E^{\rm Ox}$	$E^{\rm Red}$ *
	V	
C_{60}	—	−0.40/−0.33, −0.76/−0.71, −1.20/−1.15
C_{70}	—	−0.41/−0.35, −0.77/−0.69, −1.19/−1.11
$CymPPh_2$	1.47	—
$CymPPh_2 + PdCl_2 + C_{60}{}^{2-}$	1.05, 1.42, 1.65	−0.45/−0.39, −0.84/−0.79, −1.24/−1.17
$CymPPh_2 + PdCl_2 + C_{70}{}^{2-}$	1.10, 1.40, 1.62	−0.43/−0.37, −0.81/−0.73, −1.20/−1.12
1	1.03, 1.44, 1.62	−0.43/−0.37, −0.80/−0.75, −1.25/−1.18
2	1.03, 1.35, 1.67	−0.42/−0.36, −0.81/−0.70, −1.23/−1.15
$CpMn(CO_3)$	>1.5	—

* Potentials of direct and reverse peaks.

The $(CymPPh_2)_2PdCl_2$ complex dissolves rather slowly due to a low solubility of $PdCl_2$. Therefore, after the reactants were mixed, the mixture was left to stay for 24 h under argon. The reaction mixture was analyzed using CV from the appearance of the cathodic peak of palladium reduction ($E = -1.06$ V) and a change in the potentials of the anodic peaks in the CV curves. For example, in a solution of the initial $CymPPh_2$, the anodic peak at $E = 1.47$ V probably corresponds to the oxidation of Mn or P. However, after formation of the $(CymPPh_2)_2PdCl_2$ complex, the peak shifts toward a more anodic potential region. Scanning to the cathodic region and reverse scanning to the anodic region produce peaks corresponding to the oxidation of Pd^0 ($E = 0.08$ V)[13] and chloride ions.

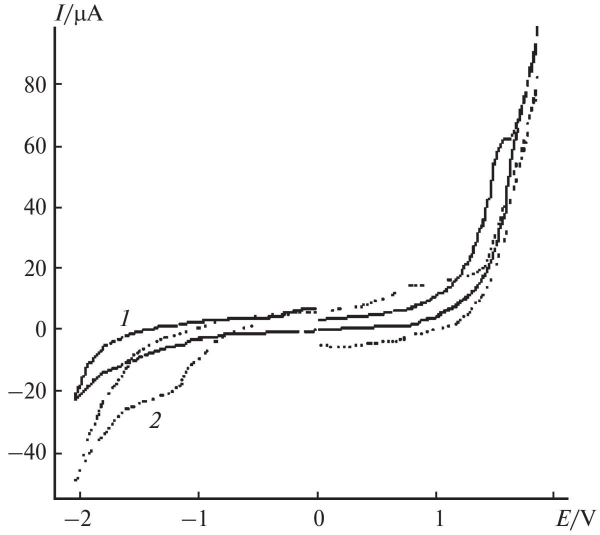

Fig. 1. CV curves for initial $CymPPh_2$ (*1*) and its complex with $PdCl_2$ ($(CymPPh_2)_2PdCl_2$) (*2*) (graphite electrode, *o*-dichlorobenzene, 0.15 *M* $Bu^n{}_4NBF_4$, Ag/AgCl/KCl).

Complexes 1 and 2. Since the solubility of complexes **1** and **2** is poor, their concentrations in a solution are low. Therefore, a graphite electrode with a high specific surface was used as the working electrode for recording CV curves. The peak potentials in the CV curves of complexes **1** and **2** in the cathodic region are almost the same as those of free C_{60} or C_{70}, respectively; they only insignificantly shift to the cathodic region (see Table 1). However, several new irreversible redox transitions appear in the anodic region as well (see Table 1 and Fig. 2). The first peak corresponds, most likely, to electron transfer involving the Pd atom

$$Pd^0 - 2\,e^- \longrightarrow Pd^{2+}.$$

Two other poorly resolved anodic peaks (see Fig. 2) probably correspond to the oxidation of the Mn- and P-containing fragments. We performed computations by the PM3(tm) method to assign the redox transitions more correctly.

Quantum-chemical calculations. In order to determine the localization of the electron changes in the oxidation and reduction of complex **1**, we calculated the molecular orbitals of this compound using the semi-empirical PM3 SCF method extended by the inclusion of parameters for all transition metals of the first row and some metals of the second and third rows. The HyperChem 6.01 program package (HyperCube, Inc., FL, USA) contains this extended method (PM3(tm)).

The geometry of the molecule (487 orbitals) was optimized with the established convergence gradi-

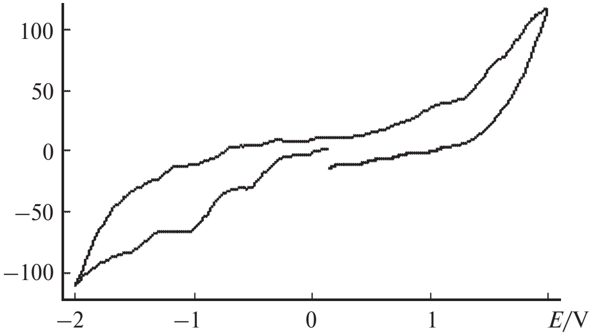

Fig. 2. CV curve for complex **1** (graphite electrode, *o*-dichlorobenzene, 0.15 *M* $Bu^n{}_4NBF_4$, Ag/AgCl/KCl).

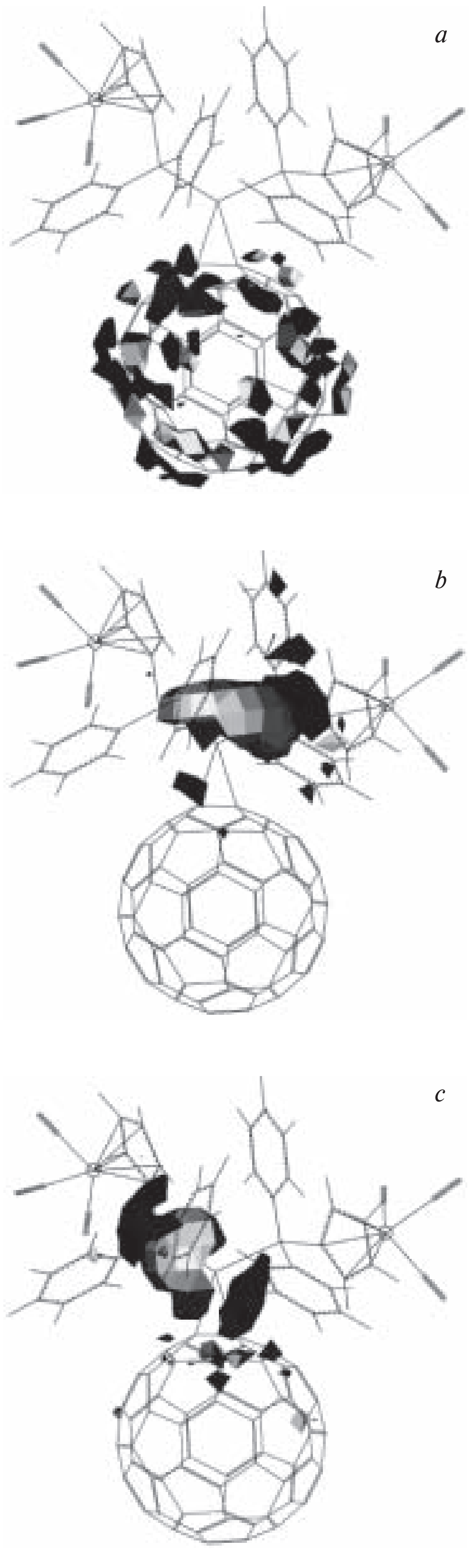

Fig. 3. Molecular orbitals of complex **1** calculated by the PM3(tm) method: LUMO (−2.63 eV) (*a*), HOMO (−6.41 eV) (*b*), and HOMO-1 (−6.95 eV) (*c*).

ent $\leq$10 cal Å^{-1}, which gives the structure shown in Fig. 3. Figure 3 also shows the frontier MO, *viz.*, the lowest unoccupied (LUMO with an energy of −2.63 eV (see Fig. 3, *a*) and two close in energy highest occupied MO (HOMO and HOMO-1 (with energies of −6.41 and −6.95 eV, respectively), see Fig. 3, *b* and *c*). It is seen that the LUMO is localized on the fullerene framework with completely no participation of the organometallic fragment, whereas the HOMO and HOMO-1 are absent on the fullerene and localized only on the P—Pd—P fragment involving no $CpMn(CO)_3$ groups. Therefore, we can assume that in the electrochemical reactions the first stage of multistage reduction involves the fullerene framework, and the first oxidation stage is localized on Pd involving no Mn-containing group.

Preparative electrolysis. A solution of $(CymPPh_2)_2PdCl_2$ was added to solutions obtained after the $C_{60}{}^{2-}$ and $C_{70}{}^{2-}$ dianions were generated in *o*-dichlorobenzene by the preparative electrochemical method (see Experimental). The formation of the fullerene-palladium complexes was proved by the CV method. The CV curves of the reaction mixtures contain the same number of cathodic and anodic peaks as the CV curves for authentic complexes **1** and **2**, and the potentials of the corresponding peaks are rather close (see Table 1). This suggests that the electrochemical synthesis really affords the exohedral complexes of [60]- and [70]fullerenes.

Thus, complexes **1** and **2** can also be obtained by our previous[**6,7,14**] method proposed for the synthesis of exohedral metal derivatives of fullerenes. However, the reaction should be carried out thoroughly to prevent the oxidation of the complex with dioxygen traces.

Electrochemical properties of ferrocenyl and cymanthrenyl complexes of [60]fullerene. It is of interest to compare the electron density distribution in two exohedral [60]fullerene complexes with similar structure, *viz.*, compound **1** and η^2-C_{60}Pd(dppf) complex studied by us previously.[**7**] The measured potentials of the oxidation and reduction peaks for these compounds and redox characteristics of their fragments are presented in Table 2.

The donor-acceptor properties of ferrocene and cymanthrene can be characterized by potentials of their oxidation and reduction. Comparison of these values (see Table 2) indicates that the cymanthrenyl group is a stronger acceptor than ferrocenyl. In addition, complex **1** contains two electron-withdrawing cymanthrenyl groups, which withdraw the electron density from the Pd atom more strongly than the ferrocenyl group does. As a result, oxidation at the Pd atom in complex **1** is considerably hindered compared to that in the ferrocenyl complex.

The reduction of the fullerene complexes involves the orbitals mainly formed from the MO of the fullerene framework. The potentials of redox transitions in the cathodic region much stronger shift to the cathodic region (compared to free C_{60}) for the ferrocenyl complex

Table 2. Potentials of the oxidation (E^{Ox}) and reduction (E^{Red}) peaks in the CV curves for complexes **1**, η^2-C_{60}Pd(dppf), and some structures similar to the fragments in complex **1** (graphite electrode, *o*-dichlorobenzene, 0.15 *M* $Bu^n{}_4NBF_4$, Ag/AgCl/KCl)

Compound	E^{Ox}	E^{Red}
	V	
η^2-C_{60}Pd(dppf)	0.87, 1.22	−0.69, −1.04, −1.52
1	1.03, 1.44, 1.62	−0.43, −0.80, −1.25
$CymPPh_2$	1.47	—
$[(Ph_2P$-η^5-$C_5H_4)]_2Fe$	0.97	—
$CpMn(CO)_3$ **15**	0.87	−2.19
Cp_2Fe **16**	0.45	−2.93

than in the case of the cymanthrenyl complex (see Table 2). The palladium bridge in cymanthrenyl complex **1** is localized between two strong electron-withdrawing fragments, *viz.*, C_{60} and $CymPPh_2$. Therefore, comparison of the reduction potentials for the exohedral complexes shows that charge transfer from the Pd atom to fullerene in the complex **1** is less significant than that in the η^2-C_{60}Pd(dppf) complex.

In the case of η^2-C_{60}Pd(dppf), the second redox transition observed in the anodic potential region corresponds to the electron transfer from the MO, whose formation is mainly contributed from the orbitals in the Fe atom.[7] The oxidation of the Mn atom is more difficult than the Fe^{II}/Fe^{III} transition in ferrocene (see Table 2). Therefore, analyzing the oxidation of complex **1**, we have to take into account two possibilities, namely, oxidation involving the AO of Mn and the AO of P. The data of quantum-chemical calculations (see above) indicate that the second redox transition is mainly localized on the orbitals mainly formed by the orbitals of the P atom. Perhaps, the electron-withdrawing CO groups in the molecule lower the orbitals of Mn, and the orbital localized on the P atom becomes HOMO-1.

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