Study of equilibria in solutions of buckminsterfullerene exohedral derivative, (η^2-C_{60})Pd(PPh_3)$_2$, using electrochemical methods and electronic spectroscopy

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Polarization curves of electrochemical oxidation and reduction, as well as electronic absorption spectra of the palladium complex of fullerene, $C_{60}Pd(PPh_3)_2$, and its mixtures with $Pd(PPh_3)_4$ have been studied in toluene—acetonitrile (9 : 1) solutions. The experimental data can be explained by the assumption that equilibrium takes place between the initial complex, polymetallated compounds, $C_{60}[Pd(PPh_3)_2]_n$ (n = 1—4), and free fullerene, C_{60}.

Key words: palladium complexes of fullerene; electrochemistry; electronic spectra.

Carbon polyhedral clusters, fullerenes, easily react with low-valent transition metal complexes, producing exohedral organometallic derivatives. Their structure and properties have been the subject of intensive investigations in recent years.[1,2] We have synthesized the Pd^0 complex with two triphenyl phosphine ligands, $C_{60}Pd(PPh_3)_2$. X-ray structural analysis of this compound showed[2] that the molecule is of C_{2v} symmetry. In this work we have studied the electrochemical and spectral features of this compound and its equilibrium transformations in solution.

Results and Discussion

Electrochemistry of $C_{60}Pd(PPh_3)_2$

Oxidation. Electrochemical measurements were carried out at the Pt-electrode in a mixture of toluene—acetonitrile (9 : 1, v/v) with 0.15 *M* Bu_4NBF_4 as a supporting electrolyte. In oxidation we observed one irreversible, diffusion controlled, two-electron wave with $E_{1/2}^{Ox}$ = 0.82 V *vs.* a saturated chlorosilver electrode (Table 1). It appears that oxidation proceeds at the atom of zero-valent palladium, *i.e.*, the main contribution to complex HOMO is made by metal d-orbitals. The rather high value of $E_{1/2}^{Ox}$ indicates that the complex studied is intermediate between Pd^0 and Pd^{II} compounds (see Ref. 3), but is closer to the latter. This is in agreement with the plane tetragonal structure of the Pd atom in the complex, which is typical for Pd^{II} complexes of electronic d^8-configuration. In oxidation free fullerene C_{60} is formed, and this was shown both electrochemically and spectrophotometrically.

Reduction. The picture observed in reduction is more complicated. As is seen from Fig. 1, *a*, the voltammogram consists of six waves, and the total current corresponds to the transfer of three electrons. The extreme current of each of the six waves has the diffusion limitation. A comparison with the voltammogram obtained in the reduction of free C_{60} under similar conditions (see Fig. 1, *b*) shows that the potentials of the first, third, and fifth peaks in the reduction of the palladium derivative

Table 1. Potentials of the reduction and oxidation waves of C_{60}, $C_{60}Pd(PPh_3)_2$, as well as the mixtures of C_{60} and $Pd(PPh_3)_4$ of various compositions (L = Ph_3P)

$C_i/10^4$ *M*			$-E_{1/2}^{Red}$	$E_{1/2}^{Ox}$
$C_{60}PdL_2$	PdL_4	C_{60}	/V	
0	0	2.13	0.34, 0.78, 1.30, 1.78, 2.30	1.76
0.68	0	0	0.34, 0.57*, 0.78, 0.99, 1.27, 1.47	0.82
0.68	0.69	0	0.57, 0.81*, 0.99, 1.25, 1.48	0.71
0.68	1.43	0	0.81, 1.01*, 1.25	0.59
0.68	2.12	0	1.05, 1.26*, 1.73	0.45
0.68	2.12	2.8	0.33, 0.57*, 0.76, 0.97, 1.31, 1.48	0.91
0.68	2.73	0	1.06, 1.26, 1.74	0.44

Note. Experimental conditions: Pt, toluene—acetonitrile , 9 : 1, 0.15 *M* Bu_4NBF_4, Ag/AgCl, 20 °C.
* The first reduction potentials of the complexes, corresponding to solution stoichiometric composition.

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almost coincide with the potentials of the first three peaks in C_{60} reduction. A similar behavior was observed earlier[4] for the complexes $C_{60}M(PEt_3)_2$ (M = Ni, Pd, and Pt). The authors accounted for the occurrence of the waves associated with C_{60} reduction by dissociation of the initial complexes, as well as their reduced forms, into a free fullerene or its corresponding reduced forms and $M(PEt_3)_2$. However, this assumption was not confirmed by our investigation.

To record the formation of $Pd(PPh_3)_2$, or more precisely $Pd(PPh_3)_2(MeCN)_n$, we used a rotating disk electrode with a ring. Setting at the disk, in turn, the potentials corresponding to the extreme current of each of the observed waves we registered the dependences of the observed ring current (i_r) on the ring potential (E_r) at E_d = const. A study of complex $Pd(PPh_3)_4$ in a toluene—acetonitrile mixture shows that its oxidation is observed at $E_{1/2} = 0.21$ V, *i.e.*, it is oxidized much easier than $C_{60}Pd(PPh_3)_2$. Since the oxidation potential of the triphenyl phosphine complexes does not depend on the number of phosphine ligands coordinated with Pd,[5] we should observe its oxidation wave at the ring electrode if $Pd(PPh_3)_2$ is formed as a result of dissociation. However, we did not observe the oxidation waves at 0.21 V though the disk electrode potential varied from 0 to −1 V. We did not succeed in attempts to find $Pd(PPh_3)_2$ chemically. Addition of phenylmercury bromide to a solution of $C_{60}Pd(PPh_3)_2$ and the study of this system by ^{31}P NMR showed that the formation of $PhPd(PPh_3)_2Br$ did not occur even on standing of this mixture for a day at the room temperature. However, the product of redox-demercurization is nevertheless formed in 7 days with a yield of 15—20 %. If the dissociation

$$C_{60}Pd(PPh_3)_2 \rightleftharpoons C_{60} + Pd(PPh_3)_2$$

was fast enough, then the addition of PhHgBr resulted in an equilibrium shift due to the fast irreversible reaction:[6]

$$Pd(PPh_3)_2 + PhHgBr \longrightarrow PhPd(PPh_3)_2Br + Hg\ .$$

These facts indicate that the dissociation mechanism[4] is doubtful in our case. At the same time, the occurrence of six reduction waves, corresponding to three-electron transfer, unambiguously indicates the equilibrium existence in solution of the complex.

One can assume the dissociation with ejection of one PPh_3 molecule:

$$C_{60}Pd(PPh_3)_2 \rightleftharpoons C_{60}PdPPh_3 + PPh_3\ . \qquad (1)$$

However, the UV-spectra analysis is inconsistent with this assumption. Waves *1*, *3* and *5*, in fact, correspond to free fullerene reduction. This is supported by the following experiment. If we bubble air through the $C_{60}Pd(PPh_3)_2$ solution, then, after deaerating the solution with Ar and registering again the voltammogram, the ratio of the wave heights changes. In oxidation of $C_{60}Pd(PPh_3)_2$ by oxygen, the free fullerene is formed. Therefore, the waves corresponding to its reduction should increase; this is, in fact, observed.

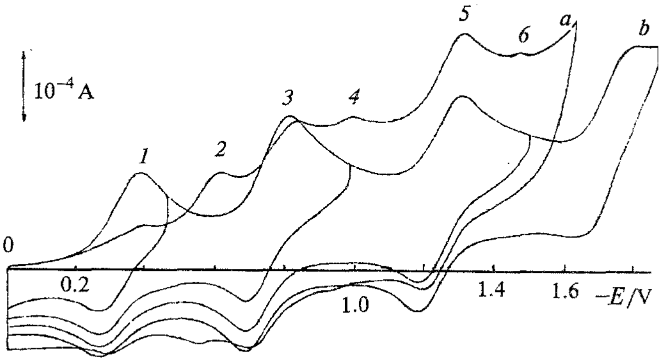

Fig. 1. Cyclic voltammograms of $2 \cdot 10^{-4}$ *M* solutions of the complex $C_{60}Pd(PPh_3)_2$ (*a*) and of C_{60} (*b*) in the mixture of toluene—acetonitrile, supporting electrolyte 0.15 *M* Bu_4NBF_4; reference electrode Ag/AgCl; potential scanning rate 200 mV s^{-1}; 20 °C.

If there is free C_{60} in solution of the initial complex, but there is no $Pd(PPh_3)_2$, one can assume the occurrence of the following equilibrium:

$$2\ C_{60}Pd(PPh_3)_2 \rightleftharpoons C_{60}[Pd(PPh_3)_2]_2 + C_{60}\ .$$

To verify this assumption we studied the effect of $Pd(PPh_3)_4$ addition on the morphology of the polarization curve. If we add one equivalent of $Pd(PPh_3)_4$ to the $C_{60}Pd(PPh_3)_2$ solution, the waves corresponding to free C_{60} disappear completely. The relative height of the reduction waves of monometallated fullerene decreases, because almost all of the complex transforms to $C_{60}[Pd(PPh_3)_2]_2$:

$$Pd(PPh_3)_4 \xrightarrow[-\ PPh_3]{} Pd(PPh_3)_3 \xrightleftharpoons[-\ PPh_3]{} Pd(PPh_3)_2\ ,$$

$$C_{60}Pd(PPh_3)_2 + Pd(PPh_3)_2 \rightleftharpoons C_{60}[Pd(PPh_3)_2]_2\ .$$

If we add to the obtained solution of bimetallic complex one more equivalent of $Pd(PPh_3)_4$, so that the ratio of Pd/C_{60} in solution becomes 1 : 3, the observed voltammogram shifts still farther to the cathode region. The waves of the monometallic complex are absent. A comparison of the voltammograms of the solutions (see Table 1), in which the ratio of Pd/C_{60} is 2, 3, and 4, indicates that in a mixture with a threefold excess of palladium in relation to fullerene there is some amount of bi- and tetrametallic complex. It is possible that disproportionation is the reason for this fact:

$$2C_{60}[Pd(PPh_3)_2]_3 \rightleftharpoons C_{60}[Pd(PPh_3)_2]_2 + C_{60}[Pd(PPh_3)_2]_4\ .$$

We believe that disproportionation can, in principle, occur in solution of $C_{60}[Pd(PPh_3)_2]_n$ by any *n* from 1 to

4. However, the equilibrium constant of reaction (2) in every case should be determined by the relative stability of the fullerene complexes formed.

$$2\ C_{60}[Pd(PPh_3)_2]_n \rightleftharpoons$$
$$\rightleftharpoons C_{60}[Pd(PPh_3)_2]_{n-1} + C_{60}[Pd(PPh_3)_2]_{n+1} \qquad (2)$$

The overall reduction current in practice does not depend on the Pd/C_{60} ratio. This can be a result of the participation of C_{60} orbitals in the reduction. The introduction of every additive group of $Pd(PPh_3)_2$ into the molecule makes reduction difficult, *i.e.*, reverse binding with participation of the palladium d-electron plays a rather substantial role and increases significantly the LUMO energy of the complex.

In Fig. 2 the reduction wave potentials attributed to the $C_{60}[Pd(PPh_3)_2]_n$ complexes are given as a function of the number of bis(triphenylphosphine)palladium groups bound with the fullerene molecule. One can see that the addition of every new group results in an $E_{1/2}{}^{Red}$ shift to the cathode region by 0.25 ± 0.01 V, *i.e.*, the group contribution is additive.

As was mentioned above, free fullerene is formed during electrochemical oxidation of the initial monometallic complex. The following observations are the electrochemical evidence of this fact. If we set at the electrode the potential corresponding to the extreme current of $C_{60}Pd(PPh_3)_2$ oxidation (0.9 V), carry out the electrolysis for one minute, and then turn on the potential scanning to the cathode region, the reduction waves of free fullerene increase considerably. In the cycle voltammogram of the solution with the Pd/C_{60} ratio equal to 3, during back scanning after trimetallic complex oxidation we registered the waves corresponding to reduction of free fullerene and of the complexes with a lesser number of palladium atoms. This indicates C_{60}—Pd bond rupture in oxidation. The triphenyl phosphine excess, introduced into solution upon $Pd(PPh_3)_4$ addition, gives the oxidation wave in the voltammogram at +1.6 V.

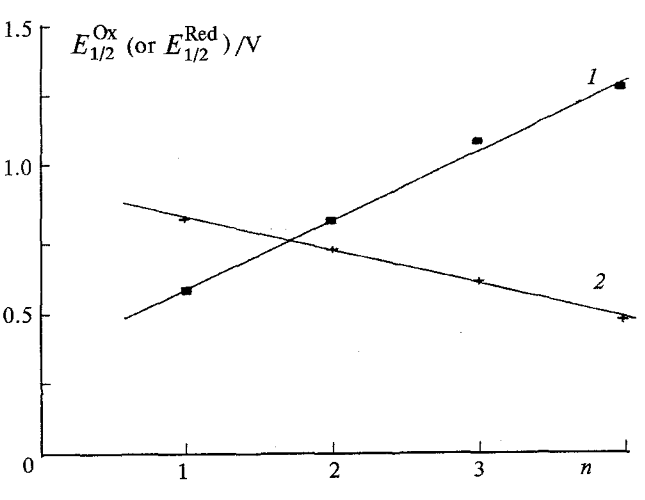

Fig. 2. Potentials of reduction (*1*) and oxidation (*2*) of the complexes $C_{60}[Pd(PPh_3)_2]_n$ (*n* = 1—4) *vs.* the number of palladium atoms (*n*) bound with the fullerene molecule.

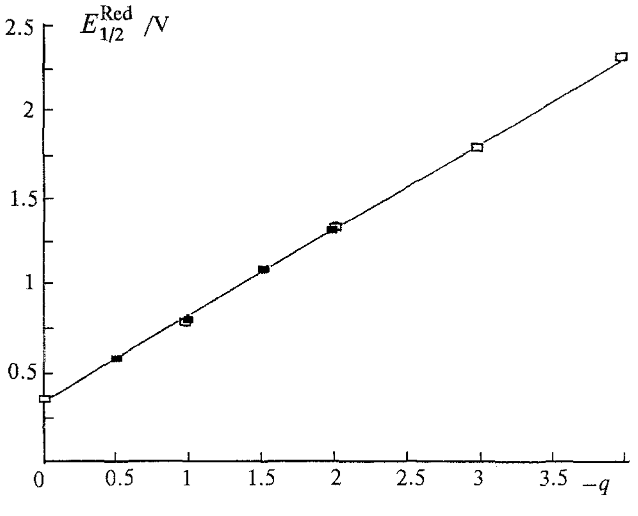

Fig. 3. Potentials of reduction of C_{60} (■) anions and of the first waves of $C_{60}[Pd(PPh_3)_2]_n$ (□) complexes *vs.* the value of the fullerene core charge.

Unlike the reduction waves, the oxidation waves of $C_{60}[Pd(PPh_3)_2]_n$ (*n* = 1—4) differ slightly. Their potentials depend poorly on *n*; the slope of line *2* in Fig. 2 is 0.11 V. This fact agrees with oxidation of the palladium atom.

In Fig. 3 the potential of every stage of C_{60} reduction (see Table 1) as a function of the charge value (*q*) of the reducing species is given. The first potential corresponds to zero charge, the second to a charge of −1 and so on. If on the line representing the dependence of the reduction potential of C_{60} and its anions on the charge, we plot the points corresponding to the expected values for the first waves of the $C_{60}[Pd(PPh_3)_2]_n$ (*n* = 1—4) reduction (dark points), we can estimate the charge value transferred from $Pd(PPh_3)_2$ to C_{60} during complexation. One can see from Fig. 3 that addition of one phosphine ligand to the fullerene molecule is equivalent to transfer of *ca.* 0.5 of the electron charge to C_{60}. Though this estimation is approximate it allows us to explain the potential shift of $C_{60}[Pd(PPh_3)_2]_n$ reduction to the cathode region with an increase in *n*, because the electronic changes in reduction are localized at C_{60}.

From Fig. 3 we can also estimate the values of the reduction potentials for $C_{60}[Pd(PPh_3)_2]_n$ complexes with *n* = 5 and 6, if they are able to exist. The half-wave potentials for these complexes should have values of −1.54 and −1.79 V, respectively. This is evident from the observed additivity of the contribution of every bis(triphenylphosphine)palladium group added.

The electronic structure of the $C_{60}Pd(PPh_3)_2$ complex and spectroscopic data

Electronic spectroscopy is a convenient method for studying the structure and the state in solution of the palladium complex of fullerene. In Table 2 the energies and the molar extinction coefficients of electronic transitions observed in the spectra of C_{60}, $C_{60}Pd(PPh_3)_2$, $Pd(PPh_3)_4$ and their mixtures are given. Using a mixture of toluene—acetonitrile (9 : 1), instead of pure toluene, the absorption band position does not change in the spectrum of the C_{60} solution, whereas the $C_{60}Pd(PPh_3)_2$ absorption bands undergo a bathochromic shift. This indicates that the bands observed in the spectra of this complex solution are charge-transfer bands, and the dipole moments of electronic transitions are of the same direction as the $C_{60}Pd(PPh_3)_2$ molecule dipole moment in the ground state.[7] It is worth noting that the spectrum of the mixture of $C_{60}Pd(PPh_3)_2$ and PPh_3 (1 : 150) in the visible region is identical to that of $C_{60}Pd(PPh_3)_2$, *i.e.*, we can assume that there is no detectable dissociation of this compound by Eq. 1. The spectrum of the $C_{60}Pd(PPh_3)_2$ solution oxidized by oxygen is identical to that of the C_{60} solution in the visible region.

To make the assignments of the bands observed in the $C_{60}Pd(PPh_3)_2$ spectra, we constructed a molecular orbital diagram. We can easily establish the level position of C_{60}, knowing the energies of electronic transition and their assignments.[8,9] The energies of HOMO can be estimated from the values of the ionization potential for C_{60}, Pd, and PPh_3.[10–12] The energies of the $^3D_3(d^9s) \leftarrow {}^1S_0(d^{10})$ and $^3P_2(d^9p) \leftarrow {}^3D_3(d^9s)$ transitions for palladium atom[13] allow us to estimate the energies of its 5s- and 5p-orbitals. The LUMO position for PPh_3 is determined by the electronic transition energy, equal to 4.768 eV.[14]

Table 2. Absorption spectra of solutions of C_{60}, $Pd(PPh_3)_2$, $C_{60}Pd(PPh_3)_2$, and their mixtures in toluene in visible and near UV regions

Compound (C_i/10^5 *M*)	$h\nu$/cm^{-1} (lg ε)
C_{60} (10÷100)	15910 (2.50), 16680 (2.81), 18500 (2.86), 23800 (2.87), 24250 sh, 24500 (3.44), 25360 sh, 26160 sh, 29700 (4.76)
C_{60} (10÷100)*	15910 (2.70), 16680 (2.92), 18500 (2.98), 23800 (3.04), 24250 sh, 24500 (3.53), 25360 sh, 26160 sh, 29700 (4.8)
$Pd(PPh_3)_4$ (10÷100)	33200 (4.0)
C_{60} (5.18), $Pd(PPh_3)_4$ (4.30)	15100 (3.63), 16300 (3.73), 22750 (3.99), 24500 sh, 25300 sh, 29700
$C_{60}Pd(PPh_3)_2$ (3.92)	15100 (3.63), 16300 (3.73), 22750 (4.00), 24500 sh, 25300 sh, 29700
$C_{60}Pd(PPh_3)_2$ (7.75)*	15000 (3.53), 16300 (3.62), 22650 (3.90), 24500 sh, 25300 sh, 29700 (4.42)
$C_{60}Pd(PPh_3)_2$ (4.68), $Pd(PPh_3)_4$ (5.20)	16550 (4.06), 18000 sh, 23000 (4.41)
C_{60} (3.45), $Pd(PPh_3)_4$ (69.0)	16500 sh, 20000 (4.48), 26000 (4.80)

* In mixture of toluene—acetonitrile (9 : 1, v/v).

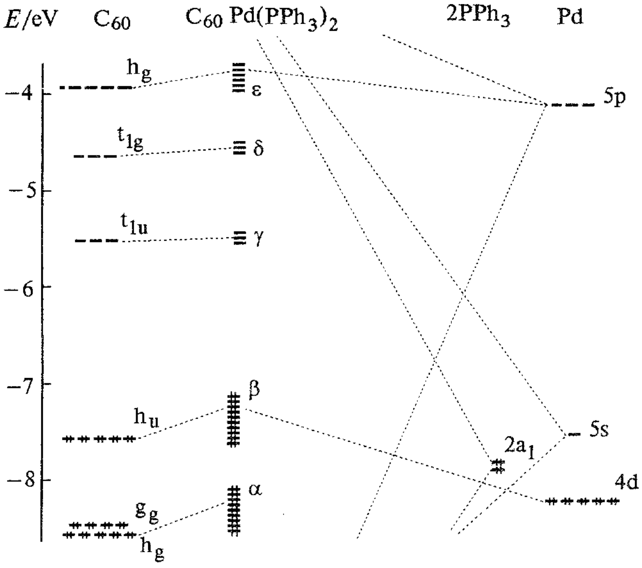

Fig. 4. Diagram of the frontier molecular orbitals of the complex $C_{60}Pd(PPh_3)_2$.
$\alpha = 3a_1 + 2a_2 + 2b_1 + 2b_2\ (h_g + g_g)$; $\beta = 3a_1 + 3a_2 + 2b_1 + 2b_2\ (h_u + \mathrm{Pd4d})$; $\gamma = a_1 + b_1 + b_2\ (t_{1u})$; $\delta = a_2 + b_1 + b_2\ (t_{1g})$; $\varepsilon = 2a_1 + a_2 + b_1 + b_2\ (h_g + b_1(\mathrm{P3p}))$.

For the $C_{60}Pd(PPh_3)_2$ molecule with C_{2v} symmetry only the orbitals that belong to representations a_1 and b_2 participate in the formation of metal—ligand bonds. The orbitals a_2 and b_1 are non-bonding.[7] The s,p,d-orbitals of the palladium atom belong to the following irreducible representations of the C_{2v} group[7].

s: a_1

p: $a_1 + b_1 + b_2$

d: $2a_1 + a_2 + b_1 + b_2$

Splitting of the C_{60} levels of I_h symmetry in $C_{60}Pd(PPh_3)_2$ complex

t_{1g}: $a_2 + b_1 + b_2$,

t_{1u}: $a_1 + b_1 + b_2$,

h_u: $a_1 + 2a_2 + b_1 + b_2$,

h_g: $2a_1 + a_2 + b_1 + b_2$,

g_g: $a_1 + a_2 + a_3 + a_4$

follows from the comparison of the tables of characters of I_h and C_{2v} irreducible representation of the groups (splitting of the C_{60} levels, determining the C_{60} spectrum in the visible and near UV region, is given).

Despite the substantial decrease in the symmetry on passing from C_{60} to the palladium complex, the geometry of the carbon skeleton changes insignificantly. By $Pd(PPh_3)_2$ complexation with fullerene the bond length C(1)—C(2) increases only by 3.8 %.[2] Therefore, the C_{60} fragment retains its effective icosahedral configuration, the relative position of C_{60} electron levels is slightly affected, and their splitting is not large (Fig. 4).

From this we can estimate the electron transition energy in the spectrum of $C_{60}Pd(PPh_3)_2$. Transitions $\gamma \leftarrow \beta$, $\delta \leftarrow \beta$, and $\gamma \leftarrow \alpha$ have to occur at frequencies of 16000 cm^{-1} (2 eV), 23000 cm^{-1} (2.8 eV), and 24000 cm^{-1} (3 eV), respectively. The last two transitions can appear in the spectrum as a single band.

The operator of the electrical dipole moment in the C_{2v} group transforms *via* three irreducible representations: A_1, B_1, and B_2.[7] Since the ground state of the $C_{60}Pd(PPh_3)_2$ molecule is described by the term $^1A_1$ (the occupied molecular orbitals are completely filled), the one-electron transitions to the states $^1A_1$, $^1B_1$, and $^1B_2$ with polarization along the axes *z, x,* and *y*, respectively, are orbital and spin allowed. Transitions between the orbitals a_1 and a_2, as well as between orbitals b_1 and b_2, are forbidden.[7]

Because allowed transitions to the states $^1A_1$, $^1B_1$, and $^1B_2$ are polarized (each one along the corresponding axis, orthogonal to the other Cartesian axes), one can assume[7] allowed transitions between nondegenerate electron levels, a_1 and a_1, a_1 and b_1 for example, being of the same probability, and, therefore, having the same dipole strength of transition *D*. From this we can estimate the ratio of D_2/D_1 for transitions $\gamma \leftarrow \beta$, $\gamma \leftarrow \alpha$, and $\delta \leftarrow \beta$.

For $C_{60}Pd(PPh_3)_2$ from $10 \cdot 3 = 30$ transitions $\gamma \leftarrow \beta$ seven transitions are forbidden by orbital selection rule. Thus, the dipole strength of transition $\gamma \leftarrow \beta$ (D_1) is 23 relative units. The number of transitions $\gamma \leftarrow \alpha$ and $\delta \leftarrow \beta$ is in total $9 \cdot 3 + 10 \cdot 3 = 57$, thirteen of which are forbidden. Hence, the dipole strength (D_2) is 44 relative units and the ratio D_2/D_1 is $44/23 = 1.91$.

Calculate the ratio of the dipole strength for transitions D_2/D_1 for the $C_{60}[Pd(PPh_3)_2]_2$ complex under the assumption that it is of C_{2v} symmetry. From $15 \cdot 3 = 45$ transitions $\gamma \leftarrow \beta$ ten transitions are forbidden; therefore, D_1 is 35 relative units; $\gamma \leftarrow \alpha$ and $\delta \leftarrow \beta$ in total are $9 \cdot 3 + 15 \cdot 3 = 72$, seventeen of which are forbidden, and so, $D_2 = 55$ relative units and the ratio $D_2/D_1 = 1.57$.

It is worth noting that if we consider the complexes $C_{60}Pd(PPh_3)_2$ and $C_{60}[Pd(PPh_3)_2]_2$ in the group C_1 or C_2 (all transitions are orbital allowed) the following results are obtained for $C_{60}Pd(PPh_3)_2$: $D_1 = 30$ and $D_2 = 57$ relative units, $D_2/D_1 = 1.90$, and for $C_{60}[Pd(PPh_3)_2]_2$: $D_1 = 45$ and $D_2 = 72$ relative units, $D_2/D_1 = 1.60$.

Thus, the ratio D_2/D_1 does not depend in practice on how the groups $Pd(PPh_3)_2$ are disposed on the fullerene surface in the complex $C_{60}[Pd(PPh_3)_2]_2$. Therefore, one can make no *a priori* assumptions relative to the structure of this complex in solution. Thus, in the $C_{60}Pd(PPh_3)_2$ spectrum we have to observe two broad absorption bands at frequencies 16000 and 23500 cm^{-1} with $D_2/D_1 = 1.91$.

Table 3. The oscillator strength and the ratio of transition dipole strengthes for mono- and dipalladium fullerenes

Compound	Oscillator strength $\gamma \leftarrow \beta$	*f* for transitions $\delta \leftarrow \beta$ and $\gamma \leftarrow \alpha$	D_2/D_1 exp.	D_2/D_1 calc.
$C_{60}Pd(PPh_3)_2$	0.084	0.20	1.67	1.91
$C_{60}[Pd(PPh_3)_2]_2$	0.19	0.41	1.55	1.57

Consider the observed spectra of the $C_{60}[Pd(PPh_3)_2]_n$ solutions. Upon complexation of the additional groups $Pd(PPh_3)_2$ with fullerene the negative charge on the fullerene increases. This makes difficult the electron transfer and results in a hypsochromic shift of the absorption bands. Therefore, we can assign the band at 15100 cm^{-1} to the $\gamma \leftarrow \beta$ transition in $C_{60}Pd(PPh_3)_2$, and the band at 16300 cm^{-1} to the $\gamma \leftarrow \beta$ transition in $C_{60}[Pd(PPh_3)_2]_2$, which is present in solution because of equilibrium (2). The band at 29700 and shoulders at 24500 and 25300 cm^{-1} in the $C_{60}Pd(PPh_3)_2$ spectrum support the occurrence of C_{60} in solution (see Table 2).

The transition $\gamma \leftarrow \beta$ occurs for $C_{60}[Pd(PPh_3)_2]_3$ at 18000 cm^{-1} and for $C_{60}[Pd(PPh_3)_2]_4$ at 20000 cm^{-1}. We also observed a similar hypsochromic shift using as an example the band corresponding to the transitions $\delta \leftarrow \beta$ and $\gamma \leftarrow \alpha$ upon introduction of an additional $Pd(PPh_3)_2$ group into the complex. This band is observed for $C_{60}[Pd(PPh_3)_2]_n$, $n = 1, 2$, at frequencies 22750—23000 cm^{-1} and for $C_{60}[Pd(PPh_3)_2]_4$ at 26000 cm^{-1}.

Because the electronic spectra for $C_{60}[Pd(PPh_3)_2]_n$, $n = 1, 2$, are well resolved, we can calculate the oscillator strength for them by equation

$$f = 4.315 \cdot 10^{-9} \int_{\nu_{min}}^{\nu_{max}} \varepsilon \, d\nu \ ,$$

where ν_{min} and ν_{max} are boundaries of the absorption band, and also the ratio of transition dipole strength:

$$D_2/D_1 = (f_2/f_1)(\nu_1/\nu_2),$$

where ν_1 and ν_2 are the maxima of the absorption bands.

The data obtained are presented in Table 3. The agreement between the experimental and calculated values of D_2/D_1 indicates that the assignment of spectral transitions was made adequately. The spectral data confirm the constructed diagram of the molecular orbitals of the $C_{60}Pd(PPh_3)_2$ complex, as well as the scheme of the equilibria between the complexes of different composition in solution, suggested on the basis of electrochemical measurements.

Experimental

Equipment and materials. The electrochemical measurements were carried out with SVA-1V-M voltammetric equipment. A platinum disk electrode with a ring had the following geometric dimensions: disk radius 2.57 mm, inner ring radius 2.65 mm, outer ring radius 3.68 mm. A platinum wire was used as an auxiliary electrode. A saturated chlorosilver electrode was used as a reference electrode. The voltammograms were registered at the following potential scanning rates: 20, 100, 200, and 500 mV s^{-1}. The electrode rotating rate was varied in the range from 1500 to 3500 rev min and the ohmic losses were considered. The electronic spectra were obtained with Specord UV-VIS and Specord NIR spectrophotometers in quartz cuvettes with optical paths of 10 and 1 mm.

Acetonitrile of analytical grade was stirred over CaH_2 for two days, then distilled from CaH_2. The solvent obtained was boiled over P_2O_5 for 3 h and then distilled from fresh P_2O_5. Toluene of analytical grade was boiled over metallic Na for 3 h and distilled.

Solution preparation. 0.494 g of Bu_4NBF_4 was introduced into a tube with a glass joint and vacuum valve. The tube was evacuated and 4 mL of toluene and 1 mL of acetonitrile preliminarily degassed were refrozen into it. The required quantity of $C_{60}Pd(PPh_3)_2$ was introduced into another tube, the tube was evacuated, and 5 mL of preliminarily degassed toluene was refrozen in it. After these procedures the vacuum system was filled with Ar. The solutions obtained were transferred into the electrolytic cell by blowing Ar; Ar was blown through for 10 min and then the electrochemical measurements were carried out. Solutions for optical measurements were prepared similarly.

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