Electrochemical oxidation and reduction of rhodium and iridium complexes with fullerenes C_{60} and C_{70}

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The electrochemical behavior of rhodium and iridium complexes with fullerenes C_{60} and C_{70} was studied by cyclic voltammetry in a THF—toluene mixture. The complexes were found to be capable of oxidation and reduction. It was demonstrated that the *in situ* generation of metallofullerene complexes in the electrochemical cell by the interaction of C_{60} and C_{70} with hydridocarbonylphosphine complexes of rhodium and iridium, $HM(CO)(PPh_3)_3$, is possible. The influence of structural factors and the action of CO_2 on changes in the redox properties of fullerene complexes was considered.

Key words: cyclic voltammetry, fullerene, iridium and rhodium hydride complexes.

In our previous works,[1–3] we showed that the interaction between hydride complexes of rhodium and iridium $HM(CO)(PPh_3)_3$, M = Rh (**1**), Ir (**2**), and $HIr(PPh_3)_2(COD\text{-}1,5)$ (COD is cyclooctadiene) with fullerenes C_{60} and C_{70} results in the formation of the compounds $(\eta^2\text{-}C_n)MH(CO)(PPh_3)_2$ (n = 60, 70) and $(\eta^2\text{-}C_{60})Ir(H)(PPh_3)(COD\text{-}1,5)$, respectively, where the metal atom is coordinated to the C_{60} molecule through the C(1)—C(2) bond and to the C_{70} molecule through the C(1)—C(9) bond. In this work, the above metallofullerenes were studied by the cyclic voltammetry (CVA) method in THF solutions and in THF—toluene mixtures.

Results and Discussion

Hydridocarbonylphosphine complexes of rhodium and iridium

Three peaks, a reversible one-electron peak, A (at 0.38 V), a one-electron irreversible peak, B (at 0.70 V), and a peak at 1.40 V corresponding to the oxidation of eliminated PPh_3 ligand (Fig. 1), are present on the cyclic voltammogram (CV) of the rhodium complex **1**, readily dissociated[4] in THF at 20 °C with elimination of the PPh_3 ligand,

$$HRh(CO)(PPh_3)_3 \rightleftharpoons HRh(CO)(PPh_3)_2 + PPh_3 \quad (1)$$

It turned out that the effects of the factors resulting in the shift of equilibrium (1) toward the undissociated form of the complex[5] (*e.g.*, the increase in the concentration from $6 \cdot 10^{-4}$ to $1 \cdot 10^{-2}$ mol L^{-1}, the addition of a 10-fold molar excess of PPh_3, as well as the decrease in the temperature to −35 °C [6]) appeared to cause no change in the potential of peak A. The results obtained suggest that the number of coordinated PPh_3-ligands in $HRh(CO)(PPh_3)_n$ (n = 2, 3) has no effect on the oxidation potentials of the complexes within the limits of sensitivity of the CVA method. This independence of oxidation potentials on the number of PPh_3 ligands has also been observed for palladium complexes $Pd(PPh_3)_n$.[7]

The oxidation peaks of complex **2**, which is incapable of dissociation in a THF solution, are analogous to peaks A and B of complex **1** (Fig. 1). The close values of the potentials of peaks A and B for **1** and **2** (Table 1) indicate that in these complexes the differences in the energies of the HOMOs participating in the oxidation process are small.

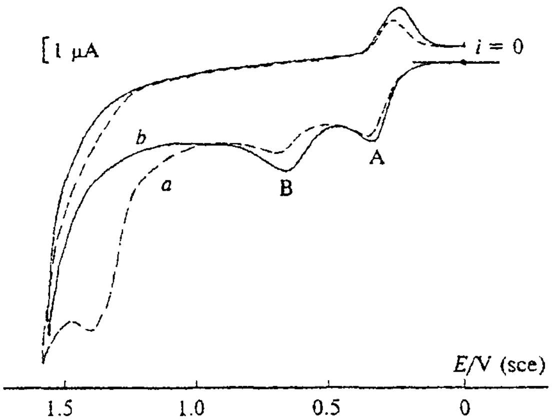

Fig. 1. Cyclic voltammograms of the oxidation of complexes $HRh(CO)(PPh_3)_3$ (*a*) and $HIr(CO)(PPh_3)_3$ (*b*) (THF, $c = 5 \cdot 10^{-4}$ mol L^{-1}).

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Table 1. Redox potentials of the rhodium and iridium complexes

Complex	E_p^{ox}/V	$-E_p^{red}$/V								
		$Ф_1$	K_1	M^a	$Ф_2$	K_2	$Ф_3$	K_3	$Ф_4$	$Ф_5$
1	1.40 0.70 0.38									
2	0.66 0.35									
3	1.13	0.30^b	0.52		[0.90	0.90]^c	1.50	1.80	2.00	2.50
4	1.22	0.30^b	0.63		0.90	1.15	1.50	1.74	2.00	2.50
5	1.20	0.30^b	0.59		0.90	1.11	1.50	1.70	2.00	2.50
C_{60}		0.30			0.90		1.50		2.00	2.50
C_{60} + **1** (1 : 2)	1.13, 0.80		0.52	[0.90	0.90	0.90]^c	1.50		2.00	2.50
3 + **1** (1 : 1)	1.13, 0.80		0.52	[0.90	0.90	0.90]^c	1.50		2.00	2.50
C_{60} + **2** (1 : 2)	1.22, 1.00			0.90		1.15	1.50	1.74	2.00	2.50
4 + **2** (1 : 1)	1.22, 1.00			0.90		1.15	1.50	1.74	2.00	2.50
C_{70}		0.28			0.85		1.36		1.85	2.50
C_{70} + **1** (1 : 1)	1.13		0.50		[0.85	0.85]^c	1.36		1.85	2.50
C_{70} + **1** (1 : 2)	1.13, 0.80		0.50	[0.85	0.85	0.85]^c	1.36		1.85	2.50
C_{70} + **2** (1 : 1)	1.22		0.63		0.85	1.13	1.36		1.85	2.50
C_{70} + **2** (1 : 2)	1.22, 1.00			0.95		1.13	1.36		1.85	2.50

[a] The first reduction peak of the bimetallic complex.

[b] The peak is due to the C_{60} impurity.

[c] Overlap of the peaks.

The results obtained are close to results reported in Ref. 6, in which electrochemical oxidation of **1** and **2** in a CH_3CN medium is described; this makes it possible to adopt the scheme of oxidation of complexes **1** and **2** suggested in the above work as a common scheme for donor aprotic solvents:

$$\mathrm{HM(CO)(PPh_3)}_n \underset{\text{peak A}}{\overset{-e}{\underset{+e}{\rightleftharpoons}}} [\mathrm{HM(CO)(PPh_3)}_n]^+ \xrightarrow[\text{peak B}]{-e,\ \mathrm{Solv}} [\mathrm{HM(CO)(PPh_3)}_n(\mathrm{Solv})]^{2+}, \tag{2}$$

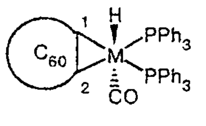
M = Rh (n = 2, 3); Ir (n = 3); Solv = CH_3CN [6], THF

According to this scheme, the oxidation of complexes **1** and **2** occurs in two successive one-electron stages and includes the formation of cationic complexes that contain Rh or Ir in oxidation state (II). It should be emphasized that no peaks of reduction of complexes **1** and **2** are present on the CVs up to potentials of −2.8 V.

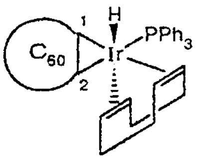
Metallofullerene complexes

Redox properties of $C_{60}HM(CO)(PPH_3)_2$ and $C_{60}HIr(PPh_3)(COD\text{-}1,5)$ complexes

The potentials of the oxidation and reduction peaks present on the CVs of metallofullerene complexes ($C_{60}Rh(H)(CO)(PPh_3)_2$ (**3**), $C_{60}Ir(H)(CO)(PPh_3)_2$ (**4**), and $C_{60}Ir(H)(PPh_3)(COD\text{-}1,5)$ (**5**) in THF, are given in Table 1. The potentials of the reduction peaks of C_n (n = 60, 70) measured under the same conditions are also listed therein.



3: M = Rh
4: M = Ir



5

Oxidation. Unlike complexes **1** and **2**, which are oxidized in two one-electron stages (Fig. 1), only one two-electron irreversible oxidation peak was observed for each of the metallofullerene complexes **3**—**5** (Fig. 2, complex **3**). The potentials of the oxidation peaks of complexes **4** and **5** are close (1.22 V and 1.20 V), whereas complex **3** is more readily oxidized (1.13 V) (Table 1). The oxidation likely involves the metal atom and results in cleavage of the bond between the metal and the fullerene ligand. Free fullerene C_{60} is one of the oxidation products; its first reversible reduction peak was observed in the potential back scan (Fig. 2). Cleavage of the C_{60}—metal bond also occurs in the oxidation of previously studied metallofullerene complexes of Ni, Pd, and Pt.[8]

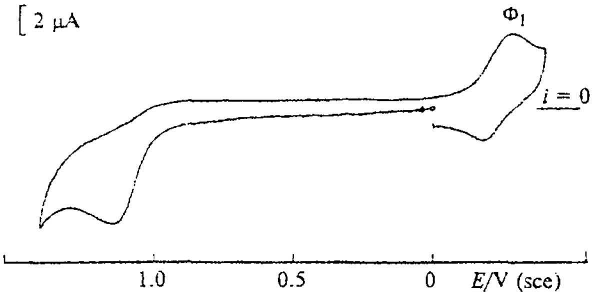


Fig. 2. Cyclic voltammogram of the oxidation of complex $C_{60}Rh(H)(CO)(PPh_3)_2$ (THF, c = 1.10^{-3} mol L^{-1}).

The oxidation of fullerenes C_{60} and C_{70} is known to occur at high positive potentials (1.76 V, benzonitrile, Bu_4NPF_6).[9] A comparison of the oxidation potentials shows that complexes **3**—**5** are oxidized much more readily than free fullerenes and with more difficulty than complexes **1** and **2**, which indicates the transfer of electron density from the metal to the fullerene ligand during complexation. The irreversible two-electron character of the oxidation of complexes **3**—**5** suggests a low stability of the intermediates, $\{C_{60}HM(CO)(PPh_3)_2\}^{+\cdot}$ or $\{C_{60}IrH(PPh_3)(COD\text{-}1,5)\}^{+\cdot}$ radical cations, whose fast subsequent chemical reaction (cleavage of the C—M bond), resulting in oxidizing, metal-containing fragments, may be one of the routes of its transformation*:

$$C_{60}HM(CO)(PPh_3)_2 \xrightarrow{-e} [C_{60}HM(CO)(PPh_3)_2]^{+\cdot} \xrightarrow{THF} C_{60} + [HM(CO)(PPh_3)_2(THF)]^{+\cdot} \xrightarrow{-e} [HM(CO)(PPh_3)_2(THF)]^{2+} \quad (3)$$

M = Rh, Ir

It should be noted that the complex $C_{60}Ir(CO)C_9H_7$ (C_9H_7 = η^5-indenyl)[10] is oxidized in one two-electron irreversible stage similarly to complexes **4** and **5**.

Reduction. New reversible peaks K_1—K_3, corresponding to the reduction of the complexes, are present on the CVs of complexes **3**—**5** along with peaks whose potentials coincide with those of the reduction peaks of free fullerene (Φ_1—Φ_5) (Fig. 3). Peak Φ_1 on the CVs of complexes **3**—**5** is very small and is likely due to a C_{60} impurity (or to the appearance of C_{60} as a result of partial decomposition of the complexes in solution). Disproportionation of complexes **3**—**5** in solution, similar to that described in detail in Ref. 11,

$$2\,C_{60}HM(CO)(PPh_3)_2 \rightleftharpoons C_{60} + C_{60}[HM(CO)(PPh_3)_2]_2, \quad (4)$$

as well as dissociation of the complexes in solution,

$$C_{60}HM(CO)(PPh_3)_2 \rightleftharpoons C_{60} + HM(CO)(PPh_3)_2 \quad (5)$$

are hardly probable, since peaks corresponding to the readily oxidizable bimetallic complex $C_{60}[HM(CO)(PPh_3)_2]_2$ or $C_{60}[HIr(PPh_3)(COD\text{-}1,5)]_2$ (see below) that should be detected along with C_{60} in the first case, and those corresponding to the oxidizable metal-containing fragment $H(CO)M(PPh_3)_2(THF)$ or $HIr(PPh_3)(COD\text{-}1,5)(THF)$ that should be found in the second case are not actually observed.

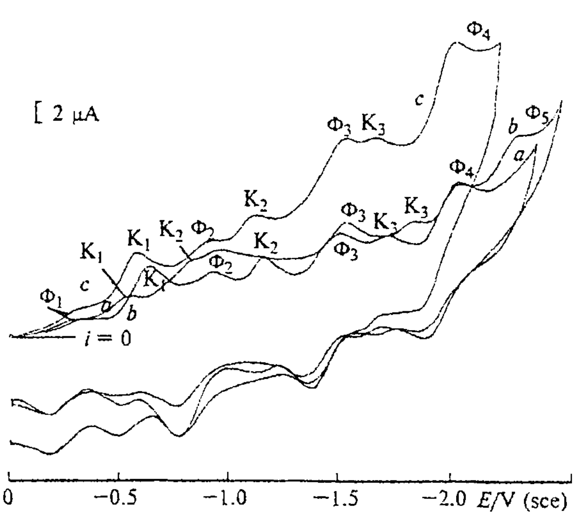


Fig. 3. Cyclic voltammograms of the reduction of complexes $C_{60}Rh(H)(CO)(PPh_3)_2$ (*a*), $C_{60}Ir(H)(CO)(PPh_3)_2$ (*b*), and $C_{60}Ir(H)(PPh_3)(C_8H_{12})$ (*c*) (THF, c = 5·10^{-4} mol L^{-1}).

The potentials of the reduction peaks of complexes **3**—**5** are given in Table 1. The appearance of the reduction peaks Φ_2, Φ_3 and Φ_4 following peaks K_1, K_2 and K_3, respectively, is evidence for partial dissociation of the reduced forms of the complexes with the formation of reduced forms of C_{60} and solvated metal-containing species $HM(CO)(PPh_3)_2$ or $IrH(PPh_3)(COD\text{-}1,5)$ (Scheme 1):

The formation of $HM(CO)(PPh_3)_2(THF)$ and $HIr(PPh_3)(COD\text{-}1,5)(THF)$ complexes in the course of reduction (Scheme 1) is confirmed by the appearance of a reversible peak of oxidation of the complex during the potential back scan (at 0.38 V for **3**, **5**, and at 0.35 V for **4**).

Three reduction peaks, K_1—K_3, are more clearly detected in the case of the iridium complex **4** (Fig. 3, *b*). Peaks K_2 and Φ_2 of complex **3** are poorly resolved (Fig. 3, *a*), as well as peaks Φ_3 and K_3 of complex **5** (Fig. 3, *c*). As can be seen from Table 1, the difference of potentials between peaks K_1 and K_2 and between peaks K_2 and K_3 for complexes **4** and **5** coincide with the differences of potentials between peaks Φ_1 and Φ_2, Φ_2 and Φ_3, and Φ_3 and Φ_4 and are approximately equal to 0.5—0.6 V. Along with the absence of the reduction peaks of complexes **1** and **2**, this fact indicates that the orbitals of the fullerene ligand are mainly involved in electron processes in the reduction of metallofullerenes, similarly to that observed in the reduction of other fullerene-containing complexes[8,10]. As can be seen in Table 1, the reduction peaks K_1 and K_3 are at more negative potentials than peaks Φ_1—Φ_3 (by 0.22, 0.33,

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* Reactions (3)—(5) and Scheme 1 are shown for complexes **3** and **4**; complex **5** undergoes analogous transformations.

Scheme 1

$$\begin{tikzcd}
C_{60}HM(CO)(PPh_3)_2 + e \arrow[r, shift left] \arrow[r, leftarrow, shift right, "\text{peak } K_1"'] & {[C_{60}HM(CO)(PPh_3)_2]^{-\cdot}} \arrow[r, "THF"] & C_{60}^{-\cdot} \arrow[d, "+e^-"] & + HM(CO)(PPh_3)_2(THF) \\
{[C_{60}HM(CO)(PPh_3)_2]^{-\cdot}} + e \arrow[r, shift left] \arrow[r, leftarrow, shift right, "\text{peak } K_2"'] & {[C_{60}HM(CO)(PPh_3)_2]^{2-}} \arrow[r, "THF"] & C_{60}^{2-} \arrow[d, "+e^-"] & + HM(CO)(PPh_3)_2(THF) \\
{[C_{60}HM(CO)(PPh_3)_2]^{2-}} + e \arrow[r, shift left] \arrow[r, leftarrow, shift right, "\text{peak } K_3"'] & {[C_{60}HM(CO)(PPh_3)_2]^{3-\cdot}} \arrow[r, "THF"] & C_{60}^{3-\cdot} & + HM(CO)(PPh_3)_2(THF)
\end{tikzcd}$$

and 0.29 V for peaks K_1 of complexes **3**—**5** and by 0.26 V for peaks K_2 of complexes **4** and **5**), which suggests the transfer of electron density from the metal to the fullerene ligand during complexation. The extent of this transfer depends on the nature of the metal atom and the ligand environment; for complexes **3**—**5** it decreases in the sequence **4** > **5** > **3**. The shift of the oxidation potentials of complexes **3** and **4** to more positive values than those of complexes **1** and **2** and the retention of the sequence order in accordance with the ease of oxidation of complexes (**4** > **5** > **3**) also agree with the above dependence. It should be noted that the transfer of electron density from the metal to the fullerene ligand occurs to a lesser extent in the case of $C_{60}Ir(CO)(\eta^5\text{-}C_9H_7)$,[10] since peaks K_1—K_3 are shifted 0.07, 0.05, and 0.09 V with respect to peaks Φ_1—Φ_3, respectively.

Thus, the results obtained show that the $C_{60}HM(CO)(PPh_3)_2$ and $C_{60}HIr(PPh_3)(COD\text{-}1,5)$ complexes are capable of both oxidation and reduction. The ion-radical species formed as a result of the transfer of an electron are reactive and enter further transformations. The stability of the radical anion species is higher than that of the radical cation species, which is in agreement with the electron-withdrawing properties of the fullerene ligand.

Redox properties of $C_{60}[HM(CO)(PPh_3)_2]_2$

Bimetallic complexes $C_{60}[HM(CO)(PPh_3)_2]_2$ were synthesized immediately in the electrochemical cell either by mixing a solution of C_{60} in toluene with a twofold excess of hydride complex **1** or **2** (as their solutions in THF) or by adding the hydride complexes **1** or **2** dissolved in THF in a 1 : 1 ratio to complexes **3** and **4**. The peaks of the oxidation of the metallofullerenes and of the eliminated PPh_3 appearing in this case on the CVs, indicate the possibility of obtaining metallofullerenes *in situ* in the electrochemical cell, while the absence of peaks of oxidation of complexes **1** and **2** confirms the completeness of their interaction with C_{60} or complexes **3**, **4**.

In addition to a peak corresponding to the oxidation of PPh_3 (at 1.40 V) and a peak whose potential coincides with that of the peak of oxidation of $C_{60}HIr(CO)(PPh_3)_2$ (at 1.22 V), a peak at lower positive potentials (1.00 V) (Fig. 4, *a*) was observed on the anodic part of CVs of solutions of the bimetallic iridium complex obtained using the above procedure; its height is equal to that of the peak at 1.22 V. The results obtained allow us to believe that the peak at 1.00 V corresponds to the oxidation of $C_{60}[HIr(CO)(PPh_3)_2]_2$ formed in the solution; the oxidative cleavage of the C—Ir bond in this complex (a peak at 1.00 V) results in the formation of $[HIr(CO)(PPh_3)_2 \cdot THF]^{2+}$ and $C_{60}HIr(CO)(PPh_3)_2$ (the peak at 1.22 V). The predominant formation of $C_{60}[HIr(CO)(PPh_3)_2]_2$ after mixing C_{60} and **2** (1 : 2) or **4** and **2** (1 : 1) was also confirmed by the analysis of the cathodic part of CV. As can be seen in Fig. 4, *b*, peak K_1, corresponding to the reduction of $C_{60}HIr(CO)(PPh_3)_2$, is absent, whereas peak M appears at −0.90 V (*cf.* Fig. 3, *b* and Fig. 4, *b*). The latter corresponds to the reduction of $C_{60}[HIr(CO)(PPh_3)_2]_2$ to the radical anion; the cleavage

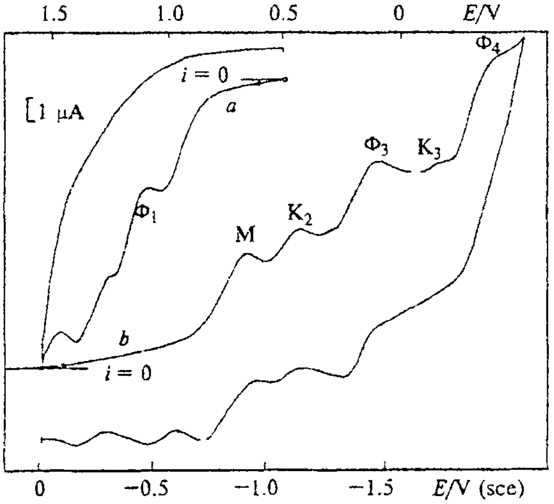

Fig. 4. Cyclic voltammograms of the oxidation (*a*) and reduction (*b*) of complex $C_{60}[HIr(CO)(PPh_3)_2]_2$: a mixture of $C_{60}Ir(H)(CO)(PPh_3)_2$ and $HIr(CO)(PPh_3)_3$ (1 : 1) in THF or a mixture of C_{60} and $HIr(CO)(PPh_3)_3$ (1 : 2) in a THF—toluene system (8 : 2).

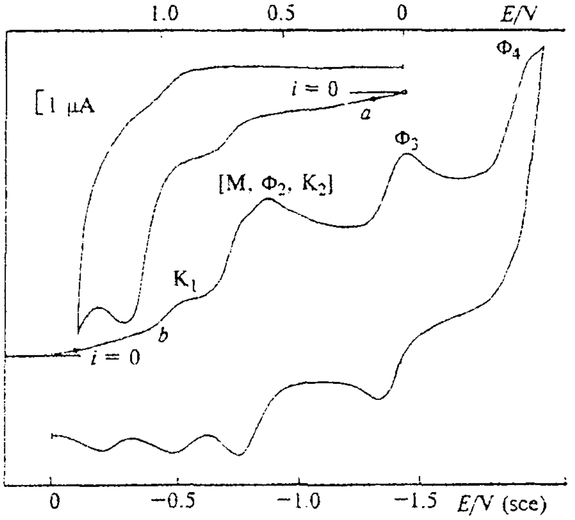

Fig. 5. Cyclic voltammograms of the oxidation (*a*) and reduction (*b*) of mixtures of C_{60} and $HRh(CO)(PPh_3)_3$ (1 : 2) in a THF—toluene system (8 : 2) or of $C_{60}Rh(H)(CO)(PPh_3)_2$ and $HRh(CO)(PPh_3)_3$ (1 : 1) in THF.

of the C—Ir bond in this complex results, in turn, in the formation of $\{C_{60}[HIr(CO)(PPh_3)_2]\}^{-\cdot}$ (peaks K_2 and K_3).

A similar picture was observed on the CV of the solutions obtained by mixing C_{60} and **1** (1 : 2) or **3** and **1** (1 : 1); however, the oxidation peak at lower positive potentials (0.80 V), which corresponds to $C_{60}[HRh(CO)(PPh_3)_2]_2$, is much smaller than the peak at 1.13 V that corresponds to oxidation of $C_{60}HRh(CO)(PPh_3)_2$ (Fig. 5, *a*). Adding excess complex **1** does not result in an increase in the height of the peak of oxidation of $C_{60}[HRh(CO)(PPh_3)_2]_2$, which indicates that $C_{60}HRh(CO)(PPh_3)_2$ is predominantly formed in solutions rather than $C_{60}[HRh(CO)(PPh_3)_2]_2$. This conclusion is confirmed by analysis of the cathodic part of the CV: it can be seen in Fig. 5, *b* that peak K_1, which corresponds to the reduction of $C_{60}HRh(CO)(PPh_3)_2$, is present while peak M in the region of −0.90 V, which corresponds to the reduction of $C_{60}[HRh(CO)(PPh_3)_2]_2$, coalesces with peaks K_2 and Φ_2. Thus, the procedure used for preparation of the metallofullerene complexes *in situ* shows the predominant formation of $C_{60}[HRh(CO)(PPh_3)_2]_2$, whereas the rhodium complexes are predominantly formed as $C_{60}HRh(CO)(PPh_3)_2$ under the same conditions.

A comparative analysis of the redox potentials of $C_{60}HM(CO)(PPh_3)_2$ and $C_{60}[HM(CO)(PPh_3)_2]_2$ (Table 1) indicates that the oxidation potentials of $C_{60}[HM(CO)(PPh_3)_2]_2$ are less positive than those of $C_{60}HM(CO)(PPh_3)_2$ by approximately 0.2—0.3 V, whereas the potentials of the reduction of $C_{60}[HM(CO)(PPh_3)_2]_2$ to the radical anion are approximately 0.3 V more negative than those of $C_{60}HM(CO)(PPh_3)_2$. Analogous differences between the redox potentials were also observed[8] for $C_{60}[Pt(PR_3)_2]_n$, (n = 1, 2; R = Et, Ph). Note that in the oxidation of $C_{60}[HM(CO)(PPh_3)_2]_2$, one fails to detect complexes containing metal atoms in different oxidation states, $[HM(CO)(PPh_3)_2]^{+\cdot}C_{60}[HM(CO)(PPh_3)_2]$, which might be due to the fast subsequent reaction of these intermediates with cleavage of the C—M bond.

Redox properties of $C_{70}[HM(CO)(PPh_3)_2]_n$ complexes

Having ascertained that the generation of $C_{60}[HM(CO)(PPh_3)_2]_n$ (M = Rh, Ir; n = 1, 2) *in situ* is possible, we used this approach to generate $C_{70}[HM(CO)(PPh_3)_2]_n$, whose electrochemical characteristics are presently unknown. On CVs of solutions obtained by adding complex **1** (or **2**) to C_{70} a peak of the eliminated PPh_3-ligand as well as peaks of oxidation and reduction were detected; the latter can be assigned to the peaks of metallofullerenes $C_{70}[HM(CO)(PPh_3)_2]_n$ (n = 1, 2) because of their resemblance to the peaks of $C_{60}[HM(CO)(PPh_3)_2]_n$.

As can be seen from the data in Table 1 and Fig. 6, only monometallic complexes $C_{70}[HM(CO)(PPh_3)_2]$ (with oxidation peaks at potentials of 1.13 V (M = Rh) and 1.22 V (M = Ir)) are formed in the interaction of C_{70} with **1** (or **2**) in a 1 : 1 ratio. Changing the C_{70} : **1** (or **2**) ratio to 1 : 2 results in the appearance of peaks at less positive potentials (0.80 V and 1.00 V for M = Rh and Ir,

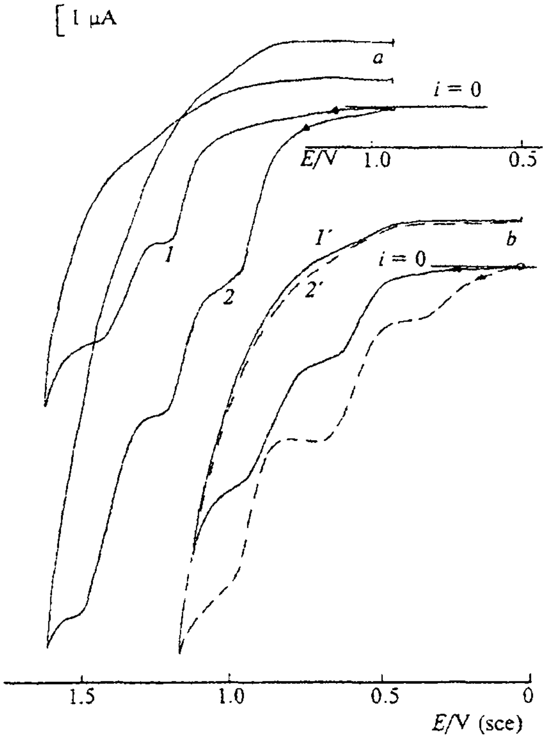

Fig. 6. Cyclic voltammograms of the oxidation of mixtures of C_{70} and $HIr(CO)(PPh_3)_3$ (*a*) and C_{70} and $HRh(CO)(PPh_3)_3$ (*b*): 1 : 1 (*1*, *1'*), 1 : 2 (*2I 2'*) (THF-toluene (8 : 2), *c* = $5\cdot10^{-4}$ mol L^{-1}).

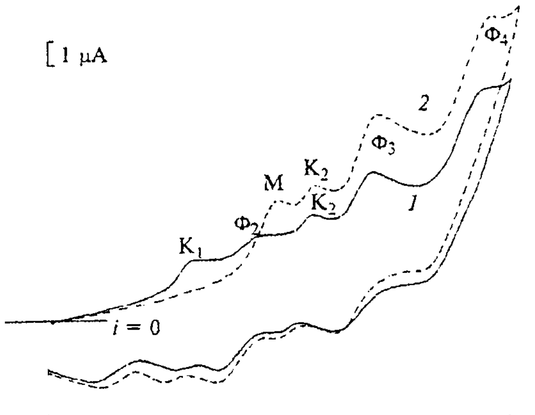

Fig. 7. Cyclic voltammograms of the reduction of mixtures of C_{70} and $HIr(CO)(PPh_3)_3$, 1 : 1 (*1*), 1 : 2 (*2*) (THF—toluene (8 : 2), $c = 5 \cdot 10^{-4}$ mol L^{-1}).

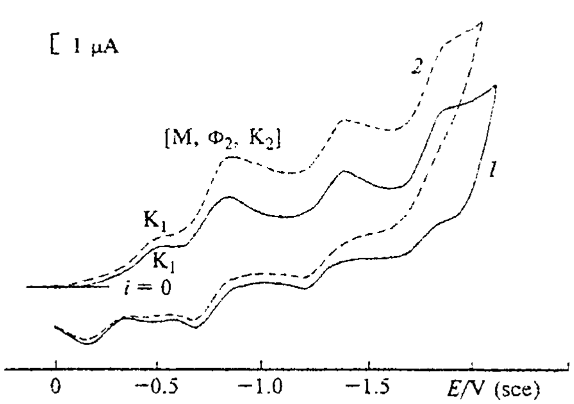

Fig. 8. Cyclic voltammograms of the reduction of mixtures of C_{70} and $HRh(CO)(PPh_3)_3$, 1 : 1 (*1*), 1 : 2 (*2*) (THF—toluene (8 : 2), $c = 5 \cdot 10^{-4}$ mol L^{-1}).

respectively) (Fig. 6, Table 1) that can be assigned to the oxidation of bimetallic complexes $C_{70}[HM(CO)(PPh_3)_2]_2$. Unlike the $C_{70}[HIr(CO)(PPh_3)_2]_2$ complex, only a small amount of $C_{70}[HRh(CO)(PPh_3)_2]_2$ complex is formed in this case in solution along with the monometallic complex $C_{70}HRh(CO)(PPh_3)_2$, which is analogous to the situation observed in the reaction of $HRh(CO)(PPh_3)_3$ with C_{60}. The same conclusion can also be drawn when considering the cathodic branches of the CVs (Fig. 7, 8). The disappearance of peak K_1, corresponding to the reduction of $C_{70}[HIr(CO)(PPh_3)_2]$, as the C_{70} : $HIr(CO)(PPh_3)_3$ ratio increases to 1 : 2 and the appearance of peak M is evidence for the presence of the bimetallic complex $C_{70}[HIr(CO)(PPh_3)_2]_2$ in solution in this case (Fig. 7). At the same time, the presence of peak K_1, corresponding to the reduction of $C_{70}HIr(CO)(PPh_3)_2$, at C_{70} : $HRh(CO)(PPh_3)_3$ ratios of 1 : 1 and 1 : 2 (Fig. 8), indicates that the monometallic complex $C_{70}HIr(CO)(PPh_3)_2$ prevails in both cases. Peak M, which corresponds to the reduction of some quantity of $C_{70}[HIr(CO)(PPh_3)_2]_2$, which is present in solution, is likely to coalesce with the successive K_2 and Φ_2 peaks, analogously to that observed for complexes of rhodium with C_{60}. As can also be seen from the data in Table 1, the potentials of oxidation and reduction of the metallofullerenes $C_{60}[HM(CO)(PPh_3)_2]_n$ and $C_{70}[HM(CO)(PPh_3)_2]_n$ are nearly equal, due to the identical electron effect of the metallofragment on the fullerene C_{60} and C_{70} cages, especially as the redox properties of C_{60} and C_{70} fullerenes taken alone coincide.[9]

Interaction of complexes 1—5 with CO_2

Taking into account the possible fixation of CO_2 by hydride complexes of transition metals,[12] we made an attempt to use the CVA method to study the interaction of complexes **1**—**5** and their oxidized and reduced forms with CO_2. Saturation of solutions of complexes **1** and **2** with carbon dioxide was found to have no effect on the CVs, which suggests that there is no interaction between either these complexes or their oxidized forms with CO_2. On the other hand, the current of peak Φ_3 becomes approximately doubled and the process of reduction becomes irreversible when solutions of complexes **3**—**5** and of the $C_{70}HM(CO)(PPh_3)_2$ complexes generated *in situ* are saturated with carbon dioxide. At the same time a new peak whose potential varies from −1.60 to −1.80 V depending on the composition of $C_nHM(CO)(PPh_3)_2$ and is less negative than the reduction potential of CO_2 (−2.30 V) appears. The results obtained and the invariability of the other peaks suggest the possibility of interaction between CO_2 and the reduced forms of metallofullerenes.

Experimental

Electrochemical measurements were performed using a PI-50-1 potentiostat. A glassy-carbon electrode (S = 2 mm^2), a platinum plate, and a saturated calomel electrode (sce) were used as the working electrode, the auxiliary electrode, and the reference electrode, respectively. Bu_4NBF_4 (0.2 *M*) was used as the supporting electrolyte, and a ferrocene—ferrocenium pair (E^0 = 0.40 V) was used as the internal standard. The rate of the potential scan was 200 mV s^{-1}.

Tetrahydrofuran and toluene were distilled over sodium benzophenone ketyl prior to use. The rhodium and iridium complexes investigated were obtained according to the procedures described in Refs. 1—3.

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