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Exohedral mono- and bimetallic hydride complexes of rhodium and iridium with C_{60} and C_{70}: syntheses and electrochemical properties

Alexander V. Usatov *, Svetlana M. Peregudova, Larisa I. Denisovich, Eugenii V. Vorontsov, Lyudmila E. Vinogradova, Yurii N. Novikov

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov St., 117813 Moscow, Russia

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Abstract

Syntheses of mono- and bimetallic hydride complexes of rhodium and iridium with fullerenes C_{60} and C_{70} are described and the results of their cyclic voltammetry (CV) studies are presented. The metal-containing $[HM(CO)(PPh_3)_2]$ moiety (M = Rh and Ir) coordinates with high stereo- and regioselectivity to the 1,2 bond of these fullerenes to form the only isomer in both cases. The attachment of the second $[HM(CO)(PPh_3)_2]$ moiety results in a complex mixture of positional and geometric isomers. Due to a high rate of formation, metallofullerene complexes may be generated in situ in the electrochemical cell. The electrochemical behavior (their redox potentials and stability of the oxidized and reduced forms) of the studied C_{60} and C_{70} organometallic derivatives with the same metal-containing fragment is identical. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Fullerenes; Rhodium; Iridium; Transition metal hydrides; Electrochemistry

1. Introduction

Notwithstanding the recent considerable progress in organometallic chemistry of fullerenes, data on electrochemical properties of fullerene complexes with transition metals are scarce [1–5]. Since the redox potentials of C_{60} and C_{70} nearly coincide [6], a comparative electrochemical study of exohedral metal complexes of both these fullerenes with the same metallofragment is of particular interest.

In this paper, our earlier results [7–9] on the syntheses of several mono- and bimetallic exohedral complexes of C_{60} and C_{70} with rhodium and iridium, as well as a characterization of their coordination geometry, stereochemistry, and electrochemical behavior are briefly discussed and analyzed together with the new data obtained.

2. Results and discussion

2.1. Syntheses of metallocomplexes

Previously [8,9], we showed that hydride complexes of rhodium and iridium $HM(CO)(PPh_3)_3$ (M = Rh and Ir) are convenient reagents for studying the coordination ability and specific features of fullerenes. First, these complexes can react with fullerenes in two different ways: (i) by a direct coordination of the metal atom to double bonds or (ii) by addition of the M–H bond to the polyene system of fullerene (Scheme 1). Secondly, the hydride ligand is a convenient 'label' that allows a reaction pathway ('i' or 'ii') to be revealed using IR and/or NMR spectroscopy. Earlier it was found [8–11] that reaction of these complexes with C_{60} and C_{70} goes exclusively via the pathway 'i' with the corresponding formation of η^2-derivatives of fullerenes. At the same time, reaction of $HRh(CO)(PPh_3)_3$ with conventional electron-acceptor olefins (e.g. tetracyanoethylene and tetrafluoroethylene) under the same conditions follows the pathway 'ii' and gives only σ-derivatives [12]. Additionally, the presence of the hydride ligand in the

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* Corresponding author.

E-mail address: usa@ineos.ac.ru (A.V. Usatov)

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fullerene metallocomplexes obtained according to pathway ‘i’ allows not only their coordination geometry, but also the coordination sites in the fullerene cage to be determined.

The mono- and bimetallocomplexes of fullerenes C_{60} and C_{70} under study were synthesized according to Scheme 2. The preparation of bimetallic derivatives is reported here in detail for the first time.

2.2. Configuration of metallocomplexes

The formation of fullerene metallocomplexes **1**–**9** as a result of substitution of one triphenylphosphine ligand in $HM(CO)(PPh_3)_3$ with a fullerene molecule is characterized by a high stereoselectivity and a retention of the mutual *trans*-arrangement of the hydride and carbonyl ligands. The latter completely determines the coordination geometry of the central metal atom in the resulting complexes.

The significant resonance interaction between ν_{CO} and ν_{RhH} observed in the IR spectra of these compounds as an ‘equalization’ of their intensities of both bands due to the close frequencies is a convincing proof of the *trans*-arrangement of the hydride and carbonyl ligands in the rhodium complexes **1** and **3** [9,12]. In the case of iridium complexes **2** and **4**, vibrational frequencies of the Ir–H and CO bonds differ significantly and the $\nu_{IrH}-\nu_{CO}$ resonance interaction was found in the comparison of their IR spectra with those for the isostructural deuterated analogues [8]. A quite analogous picture is observed in the IR spectra of bimetallic complexes **5**, **6**, and **7**. In particular, the IR bands of the mixed rhodium–iridium derivative of C_{60} **7** in the region of stretching vibrations of the M – H and CO bonds can be considered as a superposition of those for corresponding monometallic complexes (**1** and **2**).

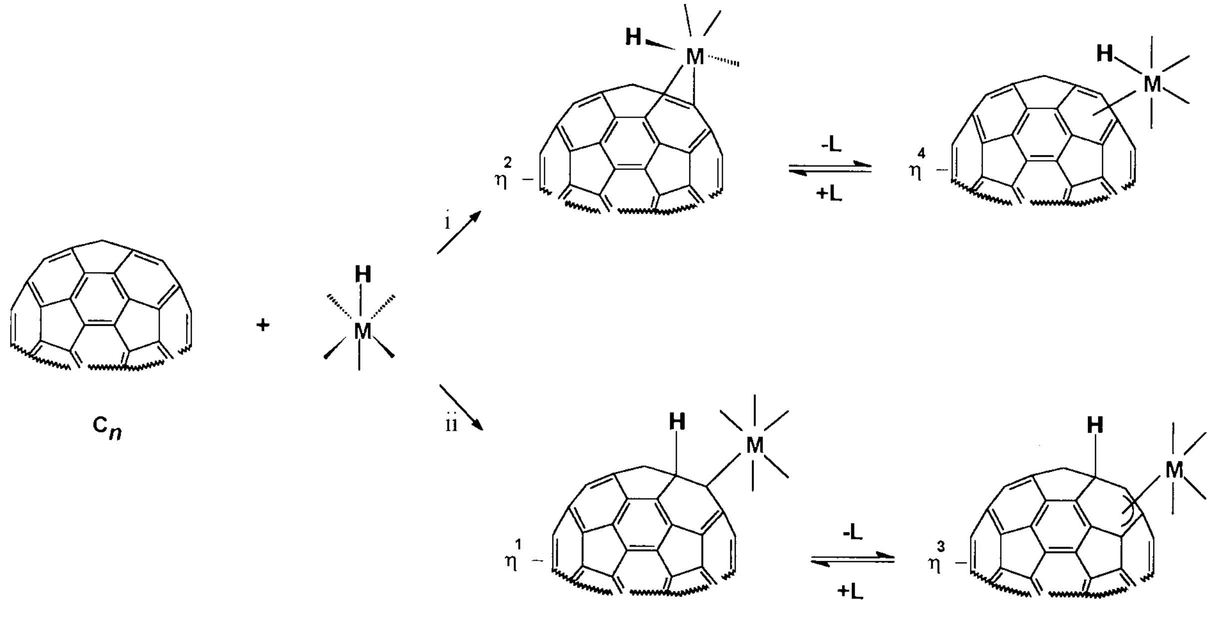
The conclusion on the configuration of metallocomplexes was also confirmed by NMR spectroscopy. For all complexes under study, hydride protons appear as triplets with small $^2J_{H,P}$ constants ($\sim$10 Hz for rhodium and 17–20 Hz for iridium derivatives) in the ^{1}H-NMR spectra. This corresponds to the *cis*-arrangement of the two triphenylphosphine ligands with respect to the hydride one. However, the coordination configuration at the transition-metal center cannot be determined unequivocally on the sole basis of NMR, since one cannot distinguish between *cis*- and *trans*-arrangements of H and CO ligands without IR data (see above).

2.3. Coordination of fullerene moiety

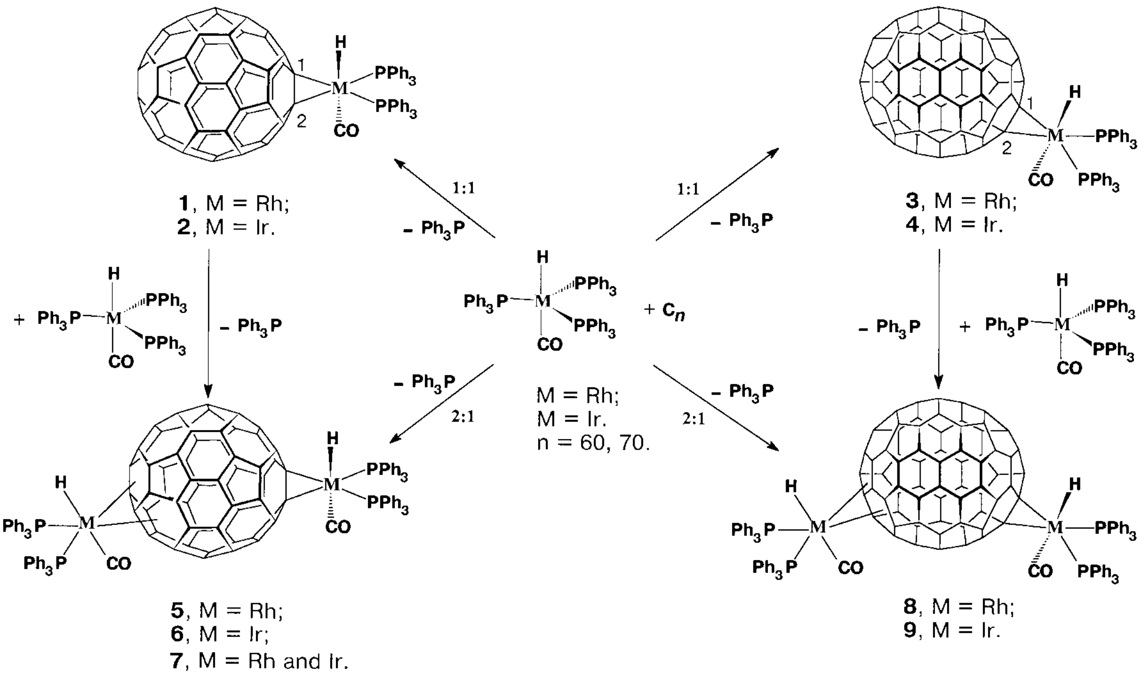
2.3.1. Monometallic complexes

A characteristic perpendicular arrangement of the hydride and phosphine ligands at the octahedrally coordinated metal atom in the complexes **1**–**4** allows the metallofragment’s position at the fullerene polyhedron to be determined. This can be done on the basis of the ^{1}H- and ^{31}P-NMR spectra of the fullerene complexes, taking into account a symmetry of all kinds of isomers considering all directions of transition-metal coordination to the fullerene cage [9].

In monometallic complexes **1** and **2**, fullerene C_{60} can be coordinated to the metal atom at the 1,2 or 1,9 bond (along 6–6 or 5–6 edge, respectively). As can be seen in Fig. 1(a), in the first case the resulting complex should exist as the only geometric isomer with the equivalent



Scheme 1.



Scheme 2.

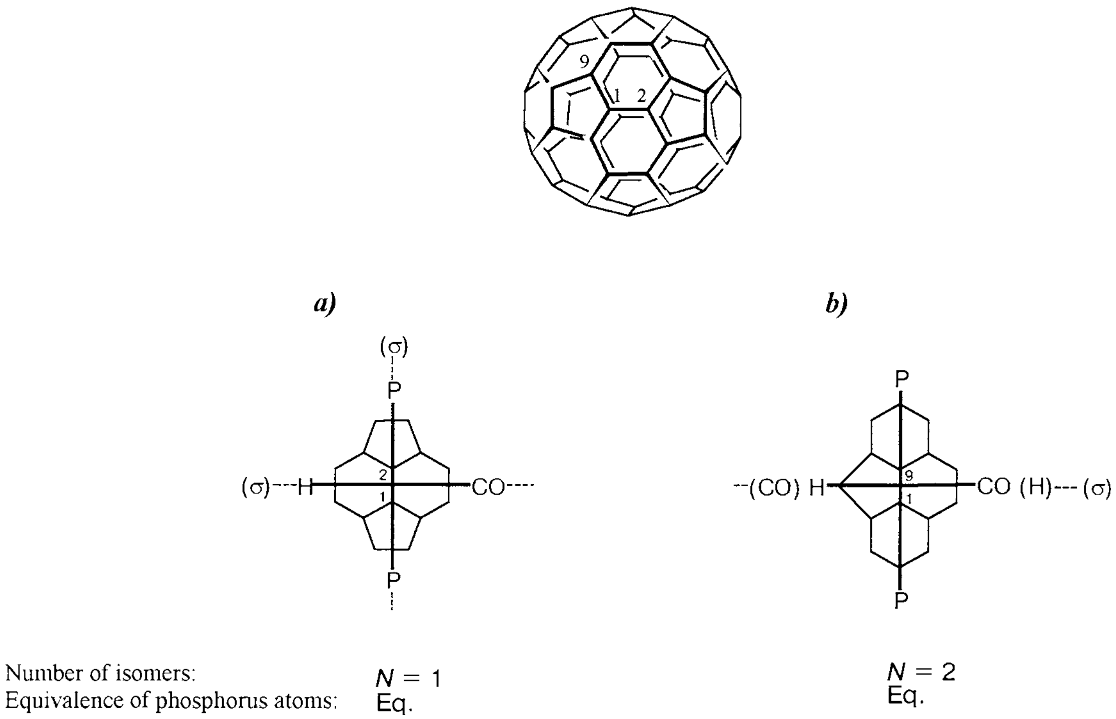


Fig. 1. A schematic representation of the positional isomers that may be formed upon coordination of the $HM(CO)(PPh_3)_2$ moiety at the 1,2 and 1,9 bonds of the C_{60} polyhedron in complexes **1** and **2**.

phosphorus atoms, whereas in the second case a 1:1 mixture of two geometric isomers, differing in the mutual arrangement of the hydride and carbonyl ligands, has to be formed. In one of these isomers, the hydride ligand is arranged opposite to the pentagon, while in the other one it is arranged opposite to the hexagon; see Fig. 1(b). The NMR patterns of these complexes, showing the presence of only one isomer, unambiguously indicate that the transition-metal atom is coordinated to the shortest 1,2 bond of C_{60} cage. This coordination is typical for all organometallic derivatives of C_{60} [13,14] studied by single-crystal X-ray diffraction.

The situation becomes drastically complicated in the case of complexes **3** and **4** due to the fact that C_{70} already contains four nonequivalent '6–6' bonds (1,2; 5,6; 7,21, and 20,21 bonds) and four nonequivalent '5–6' bonds (2,3; 5,4; 5,19, and 7,8 bonds). However, analysis of the symmetry and the number of isomers for each possible coordination site of the metal atom allows an unambiguous choice to be made even in this case. The ^{1}H- and ^{31}P-NMR spectra of the products indicate the presence of the only isomer with two nonequivalent phosphorus atoms. As can be seen in Fig. 2, it may be possible only when the metal atom is coordinated to the

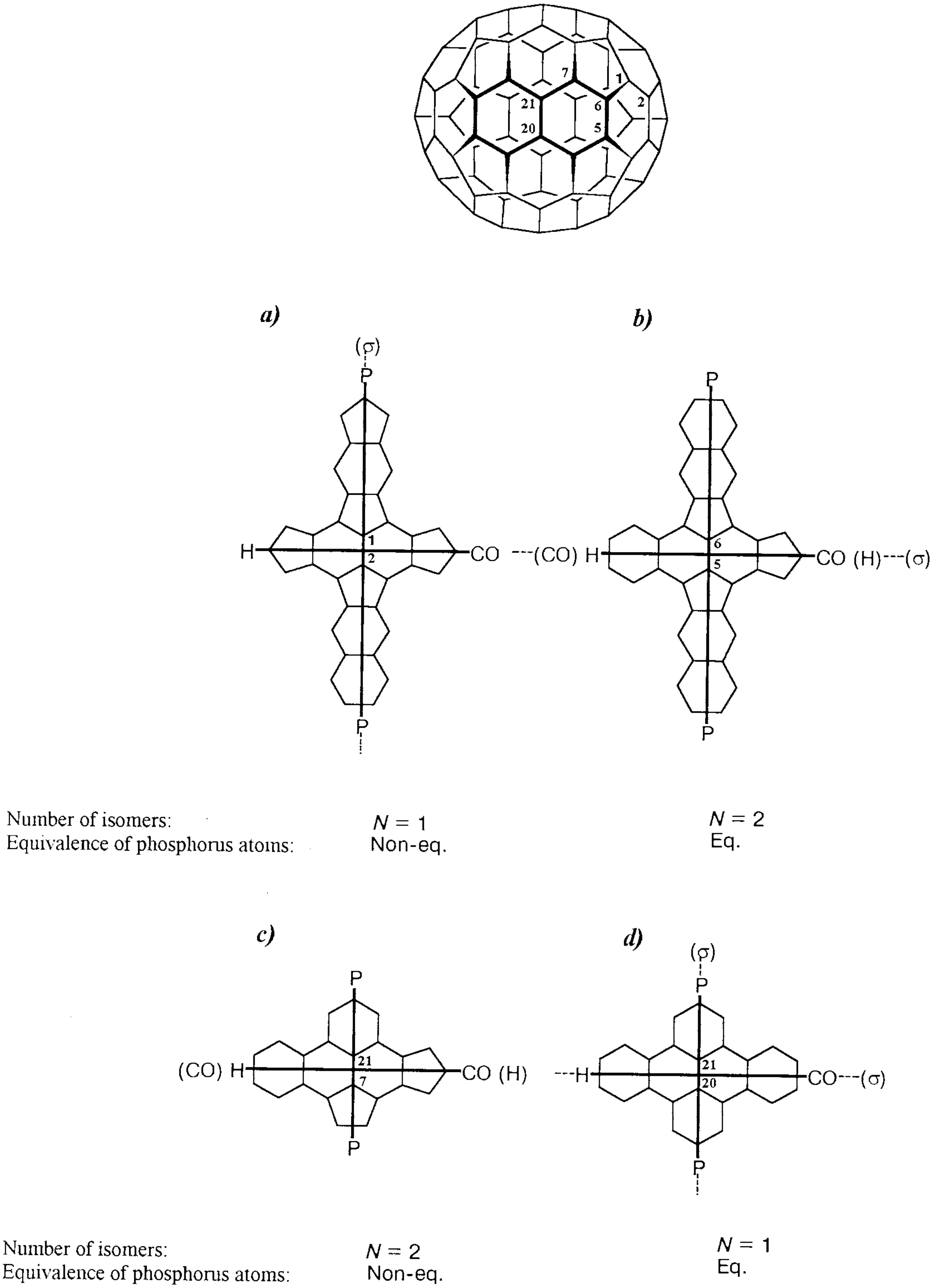


Fig. 2. A schematic representation of the positional isomers that may be formed upon coordination of the $HM(CO)(PPh_3)_2$ metallofragment at four nonequivalent 6–6 bonds of the C_{70} polyhedron in complexes **3** and **4**.

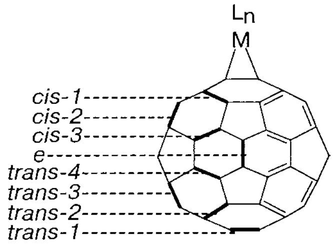
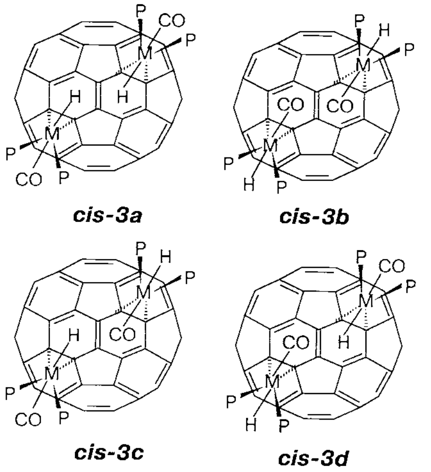


Fig. 3. The arrangement of eight 6–6 bonds at which the second metallofragment can be coordinated in the C_{60} polyhedron in monometallic complexes. Notations of the positional isomers are given.



***cis*-3a** ***cis*-3b**

***cis*-3c** ***cis*-3d**

Fig. 4. The complete set of geometric isomers for the ***cis*-3** positional isomer in bimetallic complexes.

1,2 bond of fullerene C_{70}. The possibility of coordinating the metal atom to any bond arranged along the 5–6 edges may also be ruled out, since in this case the products must always exist as 1:1 mixtures of two geometric isomers, similar to the corresponding derivatives of C_{60} (see above). The results of X-ray studies of a number of organometallic derivatives of fullerene C_{70} also indicate that the metal-containing moiety is predominantly coordinated to the 1,2 bond [13].

2.3.2. Bimetallic complexes

Since, as was shown above, transition metals are coordinated only to the 6–6 'double' bonds of fullerene C_{60}, attachment of the second $HM(CO)(PPh_3)_2$ metallofragment can theoretically result in the formation of eight different positional isomers (Fig. 3). It is obvious that only seven isomers can actually be observed, since the ***cis*-1** isomer cannot exist due to a sterical hindrance. Moreover, in bimetallic complexes **5**–**9**, because of the presence of two different ligands (i.e. hydride and carbonyl) perpendicular to the plane of the metal coordination to the double bond of fullerene at both metal atoms, each positional isomer, in its turn, gives rise to a mixture of geometric isomers differing in mutual arrangement of the hydride and carbonyl groups. Thus, in the case of homobimetallic complex **6**, both the ***trans*-1** and ***e*** isomers must be 1:1 mixtures of two geometric isomers, while all other isomers have to be 1:1:2 mixtures of three geometric isomers, as shown in Fig. 4 for the ***cis*-3** case. Here, the ***cis*-3c** and ***cis*-3d** isomers become equivalent since both metals in **6** are identical, giving rise to a double abundance of the (**c**–**d**) isomer as compared with **a** and **b** isomers. Thus, the maximum possible number of discernible isomers for the complex **6** (not considering enantiomers) must be equal to 19. The exact number of isomers in **6** is difficult to determine from the ^{31}P-NMR spectrum of this complex because of considerable overlap of a very large number of signals from nonequivalent phosphorus atoms due to the spin–spin coupling. However, the hydride region of the ^{1}H-$\{^{31}P\}$-NMR spectrum of **6** (see Fig. 5) contains 15 clearly defined

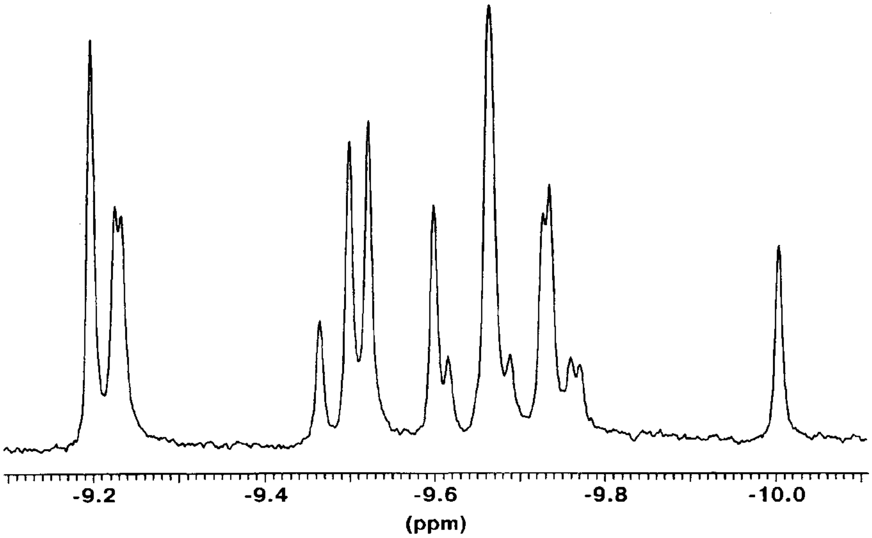


Fig. 5. The high-field region of the ^{1}H-$\{^{31}P\}$-NMR spectrum of bimetallic complex **6** in THF-d_8.

Table 1
Redox potentials of fullerene metallocomplexes

Complex	E_p^{ox} (V)	$-E_p^{red}$ (V)								
		F_1	K_1	M [a]	F_2	K_2	F_3	K_3	F_4	F_5
C_{60}		0.30			0.90		1.50		2.00	2.50
C_{70}		0.28			0.85		1.36		1.85	2.50
1	1.13		0.52		[0.90	0.90] [b]	1.50	1.80	2.00	2.50
2	1.22		0.63		0.90	1.15	1.50	1.74	2.00	2.50
3	1.13		0.50		[0.85	0.85] [b]	1.36		1.85	2.50
4	1.22		0.63		0.85	1.13	1.36		1.85	2.50
5	1.13, 0.80		0.52	[0.90	0.90	0.90] [b]	1.50		2.00	2.50
6	1.22, 1.00			0.90		1.15	1.50	1.74	2.00	2.50
7	1.22, 1.13, 0.95			0.85		1.15	1.50	1.74	2.00	2.50
8	1.13, 0.80		0.50	[0.85	0.85	0.85] [b]	1.36		1.85	2.50
9	1.22, 1.00			0.95		1.13	1.36		1.85	2.50

[a] The first reduction peak of bimetallic complex.
[b] Overlapping peaks.

resonances, which correspond to the presence of at least five positional isomers. This conclusion was drawn from the combinatorial analysis of mutual arrangement of hydride ligands, which shows that ^{1}H-{^{31}P}-NMR spectra of ***trans*-1** and ***e*** positional isomers must contain two signals of equal intensities, whereas ***cis*-2**, ***cis*-3**, ***trans*-4**, ***trans*-3**, and ***trans*-2** isomers must give four signals of equal intensities. These signals are difficult to assign to the particular isomers without additional information or separation of the isomers. In the case of heterobimetallic complex **7**, each of the positional isomers (except for the ***trans*-1** and ***e***) gives rise to a 1:1:1:1 mixture of four geometric isomers (since ***cis*-3c** and ***cis*-3d** type isomers become nonequivalent due to the presence of two different metals). The maximum total number of isomers for **7** is 24 (without considering positional ***cis*-1** isomers, as for complex **6**). However, ^{1}H- and ^{31}P-NMR data show that, unlike **6**, this complex partially dissociates (mainly with the elimination of rhodium-containing fragment) in the temperature range 190–295 K. Along with a considerable overlap of resonances, it hampers counting the actual number of isomers. Nevertheless, the ^{1}H-NMR spectral pattern in the hydride region, corresponding to Ir–H protons, indicates the presence of not less than five positional isomers. Taking into account that the integrated intensities of signals from different isomers in both cases do not differ substantially and that the total number of positional isomers is at least five, one can conclude that the attachment of the second metallofragment to the fullerene cage of monometallic complexes is characterized by a low regioselectivity, as for most organic addends [15]. This is in a drastic contrast with data on the attachment of two $Pt(PR_3)_2$ groups to the C_{60} molecule [14].

2.4. Electrochemistry

As a first step, the electrochemistry of the individual C_{60} organometallic derivatives **1, 2** and **6** was studied. Taking into account the high formation rate and stability in solution for the complexes under study [8,9], we have generated them in situ directly in the electrochemical cell. Having ascertained that the results obtained in both cases were identical, we then extended this approach to the investigation of electrochemical properties of C_{70} organometallic derivatives because their isolation in individual form is connected with a considerable loss (up to 40% weight) due to their high solubility. The results are presented in Table 1, which also exhibits the earlier data reported in Ref. [7].

2.4.1. Oxidation

2.4.1.1. Monometallic complexes. Unlike starting complexes $HM(CO)(PPh_3)_3$ ($M = Rh$, Ir) that are oxidized in two one-electron stages [7,16], only one irreversible two-electron oxidation peak is observed for monometallic fullerene derivatives **1**–**4** (a typical curve for the complex **4** is presented in Fig. 6(a)). This fact most likely indicates a low stability of intermediate $[(C_n)MH(CO)(PPh_3)_2]^{+\bullet}$ radical cation (where $n = 60$, 70) due to the strong electron-acceptor character of the fullerene ligand. Further cleavage of the metal–fullerene bond results in a fast decomposition of this radical cation that leads to free fullerene and readily oxidizable metal-containing fragments as shown in Scheme 3.

The fact that the first reversible reduction peak of fullerene (F_1) appears in the potential back scan confirms to the formation of free fullerene in the oxidation. Oxidation of rhodium complexes observed at 1.13 V occurs somewhat more easily than that of corresponding iridium analogs (at 1.22 V) (Table 1). It should be

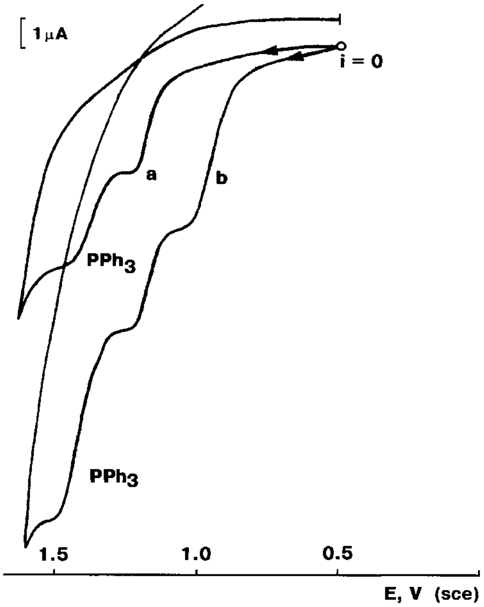


Fig. 6. Cyclic voltammograms of the oxidation of mixtures of C_{70} and $HIr(CO)(PPh_3)_3$, 1:1 (a), 1:2 (b).

noted that the observed order of ease of oxidation corresponds to the relative strength of the metal–fullerene bonding, as it was found earlier for Ni, Pd, and Pt complexes of C_{60} (Ni > Pd > Pt) [1].

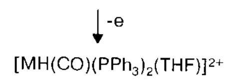
2.4.1.2. Bimetallic complexes. The anodic parts of CVs of solutions of homobimetallic complexes $(C_n)[MH(CO)(PPh_3)_2]_2$ contain a peak at 1.40 V corresponding to oxidation of PPh_3 (which was observed among the reaction products only when the complexes were generated directly in the electrochemical cell), together with a peak with the same oxidation potential as for monometallic derivative, and an irreversible two-electron peak at a smaller potential (0.80 and 1.00 V for M = Rh and Ir, respectively) (Fig. 6(b)). The latter can be considered as the oxidation peaks of bimetallic complexes.

In the case of heterobimetallic C_{60} complexes **7**, two peaks with the equal intensities characteristic for oxidation of the corresponding monometallic complexes are observed at 1.13 and 1.22 V (for M = Rh and Ir, respectively). Additionally, a new oxidation peak corresponding to the oxidation of heterobimetallic complex is observed at 0.95 V. The monometallic products can be formed either by a dissociation of the starting bimetallic complex or directly in the oxidation stage due to a dissociation of a radical cationic product. The analysis of the cathodic part of CVs of iridium derivatives **6**, **7**, and **9** (including a mixed heteronuclear complex) shows that no considerable dissociation is observed in this case. In particular, the absence of a peak corresponding to the reduction of monometallic complex (K_1) contradicts the dissociative mechanism. This is most clearly demonstrated by the example of heterobimetallic complex **7**. The anodic part of its CV contains oxidation peaks corresponding to both monometallic compounds, whereas peaks corresponding to the reduction of $(C_{60})RhH(CO)(PPh_3)_2$ are completely absent in the cathodic part. Similar observations unambiguously indicate that a dinuclear cation-radical is first formed and then rapidly and nonselectively decomposes to give two monometallic complexes, which are then oxidized at more positive potentials. At the same time, dirhodium complexes **5** and **8** dissociate considerably in a solution, and peak K_1 corresponding to the reduction of $(C_n)RhH(CO)(PPh_3)_2$ is clearly observed in the cathodic part of CVs. The fact that the oxidation peak of bimetallic complex (at 0.80 V) is much lower than that of monometallic complex (at 1.13 V) indicates that the above equilibrium can be strongly shifted toward monometallic product. It should be noted that the ratio of the peak heights remains nearly constant as an excess $HRh(CO)(PPh_3)_3$ is added.

Concluding, the oxidation of mono- and bimetallic exohedral derivatives of C_{60} and C_{70} under study is an irreversible two-electron process resulting in the bond cleavage between the transition metal atom and the fullerene cage. The oxidation potentials are dependent on the metal and the extent of metalation, but they are independent of the type of fullerene (C_{60} or C_{70}).

2.4.2. Reduction

2.4.2.1. Monometallic complexes. Along with peaks whose potentials coincide with the reduction of free fullerene (F_2–F_5), new reversible peaks (K_1–K_3) corresponding to the reduction of metallocomplexes are present on the CVs of **1**–**4** (Fig. 7 and Fig. 8(a)). Each of these peaks is shifted by 0.22–0.33 V towards more negative potentials as compared with the corresponding reduction peaks of free fullerenes (F_1–F_3) (see Table 1). The only difference observed on the CVs of the investigated C_{70} organometallic derivatives (Fig. 8(a)) as compared with similar derivatives of C_{60}, is the absence of K_3 peak, which can be due either to increased instability of the $[(C_{70})IrH(CO)(PPh_3)_2]^{2-}$ dianion or to, for in-



$$\begin{tikzcd}[column sep=small] (C_n)MH(CO)(PPh_3)_2 \arrow[r, "-e"] & {[(C_n)MH(CO)(PPh_3)_2]^+} \arrow[r, "THF"] & C_n + [MH(CO)(PPh_3)_2(THF)]^+ \arrow[d, "-e"] \\ & & {[MH(CO)(PPh_3)_2(THF)]^{2+}} \end{tikzcd}$$

Scheme 3.

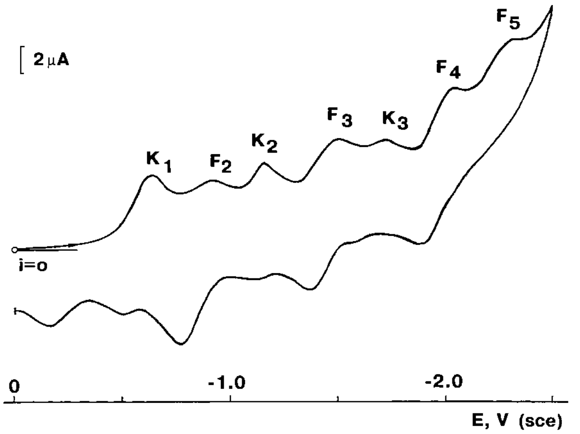


Fig. 7. Cyclic voltammogram of the reduction of complex $(C_{60})HIr(CO)(PPh_3)_2$ or a mixture of C_{60} and $HIr(CO)(PPh_3)_3$ (1:1).

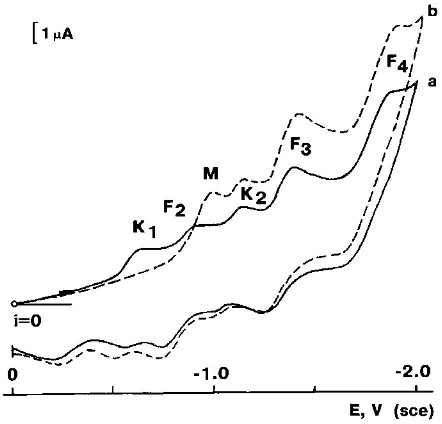
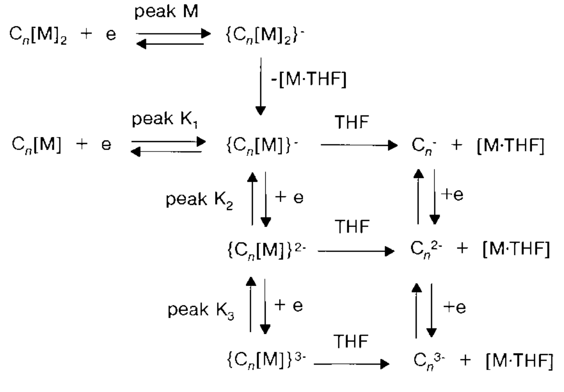


Fig. 8. Cyclic voltammograms of the reduction of mixtures of C_{70} and $HIr(CO)(PPh_3)_3$, 1:1 (a), 1:2 (b).



Scheme 4.

stance, the overlap of the K_3 and F_4 peaks. It is unlikely that the F_2–F_5 peaks of the reduction of free fullerene may appear as a result of disproportionation of the complexes **1**–**4** (Eq. (1)) (similarly to the process described in Ref. [3]) or due to dissociation of the complexes under study in solution (Eq. (2)) (as was observed for complexes of C_{60} with Pt, Pd, and Ni [1]). If so, an oxidation of bimetallic complex (C_n)-$[MH(CO)(PPh_3)_2]_2$ (in the first case) or oxidation of the metal-containing $HM(CO)(PPh_3)_2(THF)$ fragment (in the second case) would be detectable in the anodic part of the CVs. However, these peaks are not actually observed. Thus, appearance of the reduction peaks F_2–F_5 following peaks K_1–K_3 indicates that the reduced forms of the complexes partially dissociate to form corresponding fullerene anions and the solvated metal-containing particles $HM(CO)(PPh_3)_2(THF)$, as shown in Scheme 4.

$$2(C_n)MH(CO)(PPh_3) \leftrightarrows C_n + (C_n)[MH(CO)(PPh_3)_2]_2 \qquad (1)$$

$$(C_n)MH(CO)(PPh_3)_2 \overset{THF}{\leftrightarrows} C_n + HM(CO)(PPh_3)_2\cdot(THF) \qquad (2)$$

The formation of $HM(CO)(PPh_3)_2(THF)$ complexes in the reduction is confirmed by the existence of the reversible oxidation peak at the characteristic potentials (0.38 and 0.35 V for M = Ir and Rh, respectively) upon reversing the scan.

2.4.2.2. Bimetallic complexes. Cyclic voltammograms of diiridium derivatives of both fullerenes (C_n)-$[IrH(CO)(PPh_3)_2]_2$ (Fig. 9 and Fig. 8(b)) contain a reversible peak M (at -0.90 and -0.95 V for **6**, $n = 60$ and **9**, $n = 70$, respectively). This peak was attributed to the reduction of the complexes to the corresponding radical anions. Then peaks K_2, F_3, K_3, and F_4 are observed, whereas peak K_1 of the reduction of neutral monoiridium complex $(C_n)IrH(CO)(PPh_3)_2$ is absent. This indicates that only the radical anions (and not the bimetallic complexes) dissociate by the elimination of one metallofragment to give the corresponding monometallic radical anions. In their turn, all the above radical anions are further reduced according to Scheme 4 (peaks K_2 and K_3).

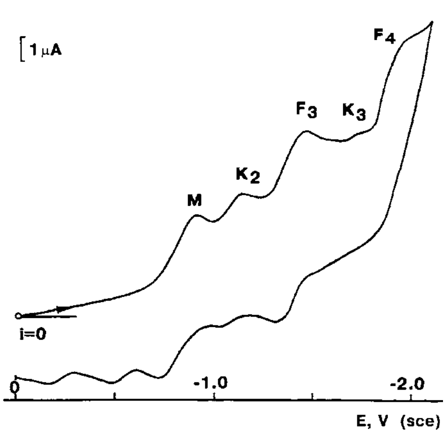


Fig. 9. Cyclic voltammogram of reduction of complex $(C_{60})[HIr(CO)(PPh_3)_2]_2$ or a mixture of C_{60} and $HIr(CO)(PPh_3)_3$ (1:2).

Generally, it may be said that the reduction of the mixed rhodium–iridium C_{60} bimetallic complex **7** oc-curs similarly to the reduction of the diiridium complex, and the radical anion formed (peak M) dissociates with the selective elimination of the rhodium-containing fragment. At the same time, it should be noted that a small peak K_1 corresponding to a reduction of neutral $(C_{60})IrH(CO)(PPh_3)_2$ is observed on the CV, which indicates that the bimetallic complex is partially dissociated with the elimination of the same rhodium-containing fragment. This fact is also confirmed by NMR spectroscopy (see above).

In the case of dirhodium derivatives of both fullerenes **5** and **8**, rather large peaks K_1 corresponding to the reduction of $(C_n)RhH(CO)(PPh_3)_2$ radical anions are observed, while peak M is almost coincident with the peaks K_2 and F_2. This confirms the conclusion made from the analysis of the anodic part of their CVs, that dirhodium complexes dissociate considerably in solution.

3. Conclusions

The interaction between fullerenes C_{60} or C_{70} and hydride complexes of rhodium and iridium $HM(CO)(PPh_3)_3$ taken in a 1:1 molar ratio occurs with high stereo- and regioselectivity to form exohedral organometallic derivatives in which the transition-metal atom is attached to the fullerene cage at the 1–2 bond in the η^2-fashion.

The attachment of the second organometallic fragment to the fullerene cage of monometallic complexes results in the formation of corresponding homo- and heteronuclear bimetallic complexes. The latter (in the case of iridium derivatives) do not dissociate in solution and exist as a mixture of at least five positional isomers (from eight of those theoretically possible for C_{60}).

A comparative analysis of the redox potentials of the studied complexes shows that the attachment of each metallofragment to the fullerene cage causes negative shifts of oxidation potentials by 0.2–0.3 V and the same shifts of ca. 0.3 V for the potentials of reduction to monoradical anion.

Both mono- and bimetallic derivatives of fullerenes C_{60} and C_{70} with the same metal-containing moiety exhibit nearly identical electrochemical patterns. This fact allows it to be suggested that the electronic perturbations, due to a pyramidalization of the carbon atoms bonded to the transition-metal atom and the corresponding transfer of the electron density from the metal atom to fullerene cage have a local character and do not result in a notable redistribution of the electron density in the rest of the molecule.

4. Experimental

All experiments were carried out under an atmosphere of dry oxygen-free argon in deoxygenation solution. The procedures for synthesis of compounds **1**–**4** and their characteristics were reported elsewhere [8,9]. Complexes **5**, **8**, and **9** were studied only in the electrochemical cell.

IR spectra were obtained on a Specord M80 spectrometer. ^{1}H-NMR spectra (400.3 MHz) and ^{31}P-{^{1}H}-NMR spectra (160.02 MHz) were recorded on a Bruker AMX-400 spectrometer relative to TMS (internal standard) and 85% H_3PO_4 (external standard), respectively.

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 ($E° = 0.40$ V) was applied as the internal standard. The rate of the potential scan was 200 mV s^{-1}.

4.1. Preparation of $(C_{60})[IrH(CO)(PPh_3)_2]_2$ (**6**)

4.1.1. Procedure A

$HIr(CO)(PPh_3)_3$ (8.5 mg, 0.0085 mmol) was added to a solution of C_{60} (6.0 mg, 0.0083 mmol) in toluene (5 ml), and the mixture was stirred at room temperature (r.t.). After 2 h, extra 8.5 mg of the iridium complex was added, the mixture was additionally stirred for 4 h, and the product was precipitated with methanol (20 ml). The reaction mixture was allowed to stay overnight. The residue was separated, washed with methanol, and dried in vacuo to obtain complex **6** (15.0 mg, 82%).

4.1.2. Procedure B

A solution of $HIr(CO)(PPh_3)_3$ (20.0 mg, 0.02 mmol) in benzene (1 ml) was added to a solution of monoiridium complex of C_{60} (**2**) (30.0 mg, 0.02 mmol) in benzene (9 ml), and the mixture was stirred at r.t. After 45 min, methanol (30 ml) and pentane (50 ml) were successively added. The residue was filtered off, washed with pentane, and dried in vacuo to obtain complex **6** (26.5 mg, 60%) as a nearly black powder. ^{1}H-NMR (THF-d_8), δ (ppm): -9.00 (t, $^2J_{PH} = 17$ Hz), -9.025 (t, $^2J_{PH} = 17$ Hz), -9.03 (t, $^2J_{PH} = 17$ Hz), -9.26 (t, $^2J_{PH} = 17$ Hz), -9.30 (t, $^2J_{PH} = 17$ Hz), -9.32 (t, $^2J_{PH} = 17$ Hz), -9.40 (t, $^2J_{PH} = 17$ Hz), -9.41 (t, $^2J_{PH} = 17$ Hz), -9.46 (t, $^2J_{PH} = 17$ Hz), -9.49 (t, $^2J_{PH} = 17$ Hz), -9.525 (t, $^2J_{PH} = 17$ Hz), -9.53 (t, $^2J_{PH} = 17$ Hz), -9.56 (t, $^2J_{PH} = 17$ Hz), -9.57 (t, $^2J_{PH} = 17$ Hz), -9.80 (t, $^2J_{PH} = 17$ Hz). ^{31}P-{^{1}H}-

NMR (THF-d_8), δ (ppm): 8.4–14.1. IR (KBr), ν (cm^{-1}): 1983 (CO), 2102 (IrH). Anal. Calc. for $C_{134}H_{62}O_2P_4Ir_2$: C, 72.75; H, 2.82; P, 5.60%. Found: C, 71.72; H, 2.66; P, 5.04%.

*4.2. Preparation of (C_{60})[RhH(CO)(PPh_3)$_2$]-[IrH(CO)(PPh_3)$_2$] (**7**)*

A solution of $HIr(CO)(PPh_3)_3$ (20.0 mg, 0.02 mmol) in benzene (1 ml) was added to a solution of monorhodium complex of C_{60} (**1**) (28 mg, 0.02 mmol) in benzene (9 ml), and the mixture was stirred at r.t. After 90 min, methanol (20 ml) and pentane (20 ml) were successively added. The residue was filtered off, washed with methanol and pentane, and dried in vacuo to obtain complex **7** (30.0 mg, 71%) as a nearly black powder. IR (KBr), ν (cm^{-1}): 1981 (CO), 2055 (RhH), 2099 (IrH). Anal. Calc. for $C_{134}H_{62}O_2P_4RhIr$: C, 75.81; H, 2.94; P, 5.84%. Found: C, 75.59; H, 2.97; P, 5.01%.

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