

# Organometallic hydrides as reactants in fullerene chemistry. Interaction of the fullerenes $C_{60}$ and $C_{70}$ with $HM(CO)(PPh_3)_3$ ( $M = Rh$ and $Ir$ ) and $HIr(C_8H_{12})(PPh_3)_2$

Alexander V. Usatov\*, Konstantin N. Kudin, Eugenii V. Vorontsov,  
Ludmila E. Vinogradova, Yurii N. Novikov

*A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russia*

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## Abstract

The interaction of the fullerenes  $C_{60}$  and  $C_{70}$  with the rhodium and iridium hydride complexes  $HM(CO)(PPh_3)_3$  ( $M = Rh$  and  $Ir$ ) and  $HIr(COD)(PPh_3)_2$  occurs with high regio- and stereoselectivity (via substitution of one triphenylphosphine molecule), and leads to the formation of only  $\eta^2$ -derivatives  $(\eta^2-C_n)MH(CO)(PPh_3)_2$ , where  $n = 60$  or  $70$  and  $(\eta^2-C_{60})IrH(C_8H_{12})(PPh_3)$  respectively. The coordination geometries of the complexes were established by IR and NMR spectroscopies. It was demonstrated that the transition metal atom in these complexes is coordinated with the  $C_{60}$  molecule at the 1,2 bond, and with the  $C_{70}$  molecule at the 1,9 bond.

**Keywords:** Rhodium; Iridium;  $C_{60}$ ;  $C_{70}$ ; Organometallic hydrides

## 1. Introduction

The investigation of the reactivity of fullerenes towards various transition metal complexes provides important information on the structure and chemical behavior of these weakly conjugated electron accepting polyenes [1–27]. Organometallic hydrides can react with fullerenes in two essentially different ways: (i) by direct coordination of the metal atom at the double bonds with formation of  $\pi$ -complexes of even hapticity; (ii) by the addition of an M–H bond to the fullerene polyene system with formation of odd hapticity complexes (Scheme 1). In addition, the hydride ligand may be of use as an unusual ‘‘label’’, providing information on both the direction of the reaction (pathways (i) and (ii)) and the structure of the resulting complexes (pathway (i)) on the basis of IR and/or NMR data.

In this paper we summarize both our earlier results

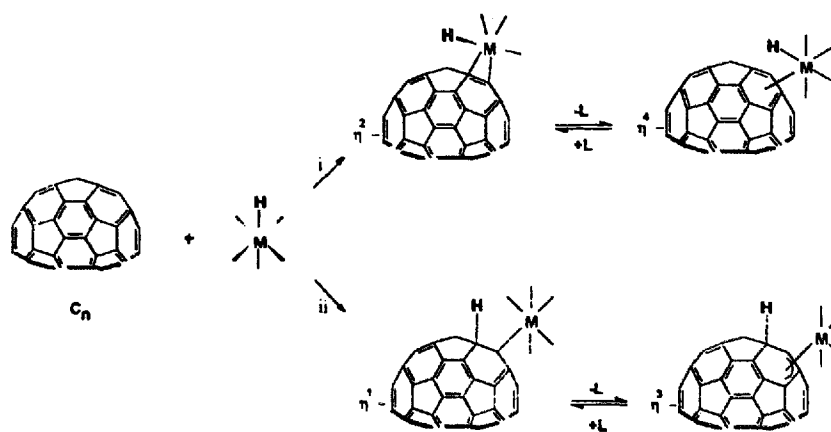
[26,27] and the new data on interaction of the fullerenes  $C_{60}$  and  $C_{70}$  with a number of rhodium and iridium hydride  $d^8$  complexes. An efficient method for determining the position in the fullerene moiety where coordination of the metal atom takes place is achieved by the analysis of  $^1H$  and  $^{31}P$  NMR spectra without resorting to X-ray studies.

## 2. Results and discussion

The mixed hydride carbonylphosphine complexes of rhodium and iridium such as  $HM(CO)(PPh_3)_3$  ( $M = Rh$  (1) and  $Ir$  (2)) react with the fullerenes  $C_{60}$  and  $C_{70}$  by pathway (i) with high regio- and stereoselectivity, giving in high yield the complexes  $(\eta^2-C_n)MH(CO)(PPh_3)_2$  (3 ( $n = 60$ ,  $M = Rh$ ); 4 ( $n = 60$ ,  $M = Ir$ ); 5 ( $n = 70$ ,  $M = Rh$ ) and 6 ( $n = 70$ ,  $M = Ir$ ), containing an  $\eta^2$ -coordinated fullerene molecule (Scheme 2).

The course of the reaction may be followed by means of UV spectroscopy (especially in the reactions

\* Corresponding author.



Scheme 1.

of fullerene  $C_{60}$  where a new band arises at 435 nm), IR spectroscopy (observing changes in  $\nu_{CO}$  and  $\nu_{MH}$  bands),  $^1H$  NMR (observing changes in resonance of the hydride proton) and  $^{31}P$  NMR spectroscopy. The data demonstrate that in all cases under consideration only one product is formed. This product can be isolated from the reaction mixture by precipitation with methanol and/or pentane.

It should be noted that the reaction of  $C_{60}$  or  $C_{70}$  with  $HRh(CO)(PPh_3)_3$  is the first example of fundamentally different reactivity of these fullerenes towards metallocenes, as compared with common electron-acceptor alkenes (such as tetrafluoroethylene and tetracyanoethylene) which react with **1** via insertion of an alkene in an  $Rh-H$  bond to form only the related  $\sigma$ -complexes [28].

The iridium hydride **7** containing phosphine and cyclooctadiene ligands in the coordination sphere can in principle react with fullerene  $C_{60}$  according to pathway (i) via two routes: substitution of triphenylphosphine or cyclooctadiene respectively. However, in this case only the replacement of the triphenylphosphine molecule takes place with formation of the exohedral derivative **8** with  $\eta^2$  bonding shown in Scheme 3.

It is particularly remarkable that the rate of reaction of the complexes under consideration with the fullerenes  $C_{60}$  and  $C_{70}$  does not depend on the type of fullerene

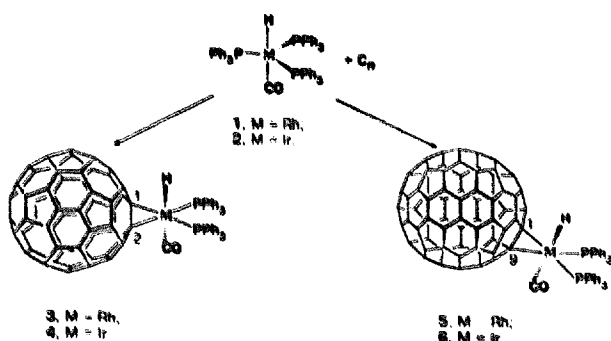
and increases in the following sequence:  $7 \ll 2 < 1$ , consistent with the ease of the dissociation of phosphine ligand in the starting complexes [28].

### 2.1. Configuration of the resulting complexes

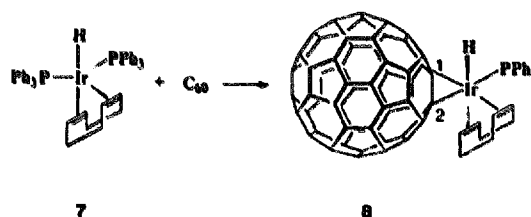
The presence of the hydride makes it possible to readily determine the coordination geometry of the central metal atom in the complexes **3–6** and **8** from the IR and/or NMR spectroscopic data. In the case of **3–6** IR spectroscopy is the more efficient method.

The resonance coupling between two vibrations  $\nu_{CO}$  and  $\nu_{MH}$  in the hydridocarbonyl complexes **3–6** is good evidence that the hydride and carbonyl ligands are in a *trans*-position [28–30]. This fact completely determines the total configuration of these complexes. In the rhodium derivatives **3** and **5** the coupling manifests itself in "equalizing" of the intensities of the  $\nu_{CO}$  and  $\nu_{RH-H}$  bands [27] due to the close frequencies of both vibrations (Fig. 1(a,b)). In the case of the iridium derivatives **4** and **6** the frequencies of the vibrations of the  $Ir-H$  and  $C-O$  bonds are significantly different, nevertheless, the presence of the  $\nu_{CO}-\nu_{IrH}$  coupling is proved by the shift of a  $\nu_{CO}$  band by 21–22  $cm^{-1}$  observed in the IR spectra of the isostructural deuterium complexes ( $\eta^2-C_n$ ) $MD(CO)(PPh_3)_2$  **9** ( $n = 60$ ) and **10** ( $n = 70$ ), which were prepared in the same manner (Fig. 1(c,d)).

These conclusions are also supported by the NMR data. In the  $^1H$  NMR spectra of the complexes **3–6** the signal assigned to the hydride proton is observed as a



Scheme 2.



Scheme 3.

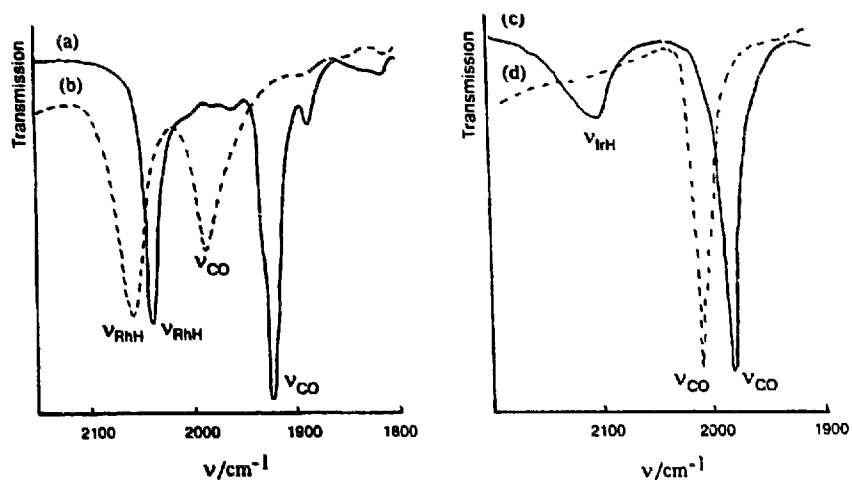


Fig. 1. IR spectra of (a)  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  in Nujol mull; (b)  $(\eta^2\text{-C}_{60})\text{RhH}(\text{CO})(\text{PPh}_3)_2$  in KBr; (c)  $(\eta^2\text{-C}_{60})\text{IrH}(\text{CO})(\text{PPh}_3)_2$  in KBr; (d)  $(\eta^2\text{-C}_{60})\text{IrD}(\text{CO})(\text{PPh}_3)_2$  in KBr.

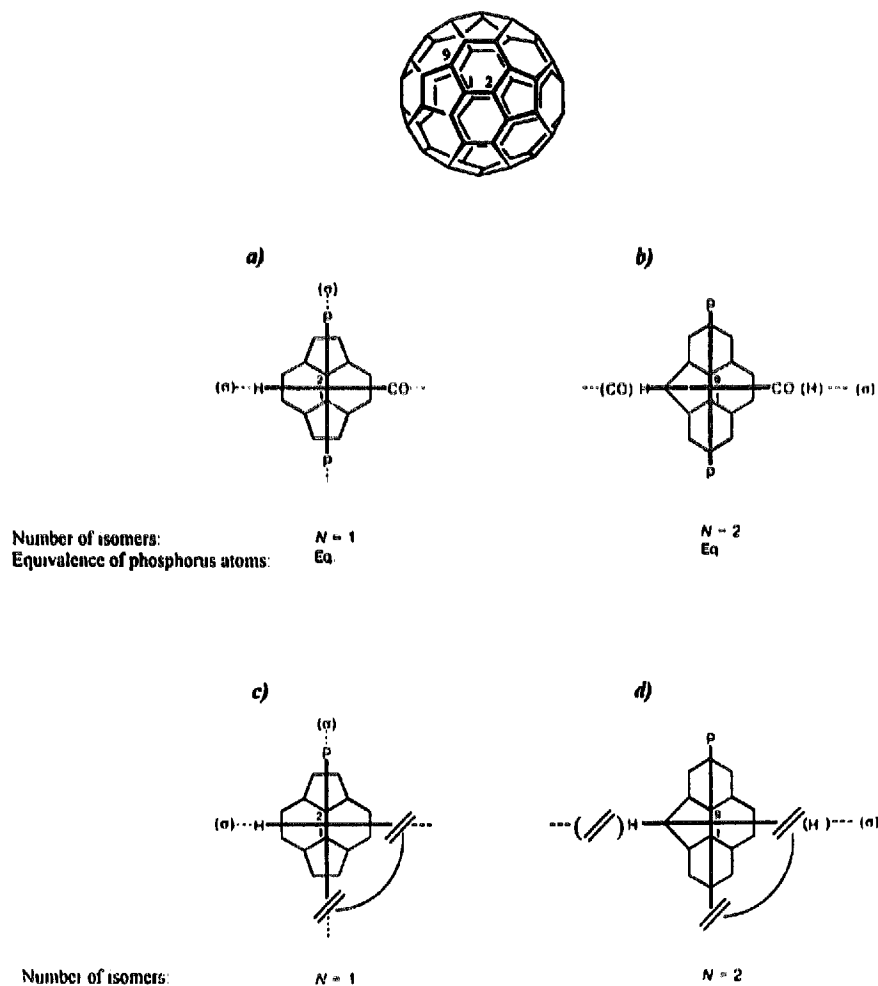


Fig. 2. The projection of a fragment of the  $\text{C}_{60}$  polyhedron along the  $\text{H-M-CO}$  and  $\text{P-Ir-P}$  bonds in complexes 3, 4 and along the  $\text{H-Ir-(HC=CH)}$  and  $\text{P-Ir-(HC=CH)}$  bonds in complex 8 showing the planes of symmetry ( $\sigma$ ), the number of possible geometric isomers ( $N$ ), and the equivalence of the phosphorus atoms in the cases where the metal is bonded to a fullerene moiety through a 1,2 bond (a,c) or through a 1,9 bond (b,d) respectively.

triplet with a small value of the  ${}^2J_{\text{H,P}}$  constant. This fact confirms that the two phosphine ligands are in *cis*-positions relative to the hydride proton [28,31]. The configuration of the cyclooctadiene complex **8** can also be established from  ${}^1\text{H}$  NMR data. In this case a doublet at  $-14.35$  ppm with  ${}^2J_{\text{H,P}} = 20.6$  Hz corresponds to the hydride proton. The observed multiplicity and the magnitude of the  ${}^2J_{\text{H,P}}$  spin-coupling constant attest to the fact that the hydride and phosphine ligands are in *cis*-positions. In addition the values of the chemical shifts assigned to the hydride proton are close in the resulting complex **8**, as well as in **7**, and in the starting complex **7** ( $-13.41$  ppm, t,  ${}^2J_{\text{H,P}} = 20.0$  Hz). This suggests that the hydride ligand in complex **8** is in *trans*-position relative to a double bond of cyclooctadi-

ene, because the ligand in the *trans*-position greatly influences the value of the chemical shift in the hydride complexes [28,31].

## 2.2. Direction of the coordination

The inherent configuration of complexes **3–6** and **8** (with hydride and phosphine ligands in orthogonal planes) allows one to determine the bond in the fullerene polyhedron that is involved in coordination with the transition metal atom. It can be done from  ${}^1\text{H}$  and  ${}^{31}\text{P}$  NMR data taking into account the number of possible isomers and their symmetry.

Thus, in complexes **3** and **4** fullerene  $\text{C}_{60}$  may be coordinated with the transition metal atom either through a 5–6 edge, i.e. at the 1,9 bond, or through a 6–6 edge,

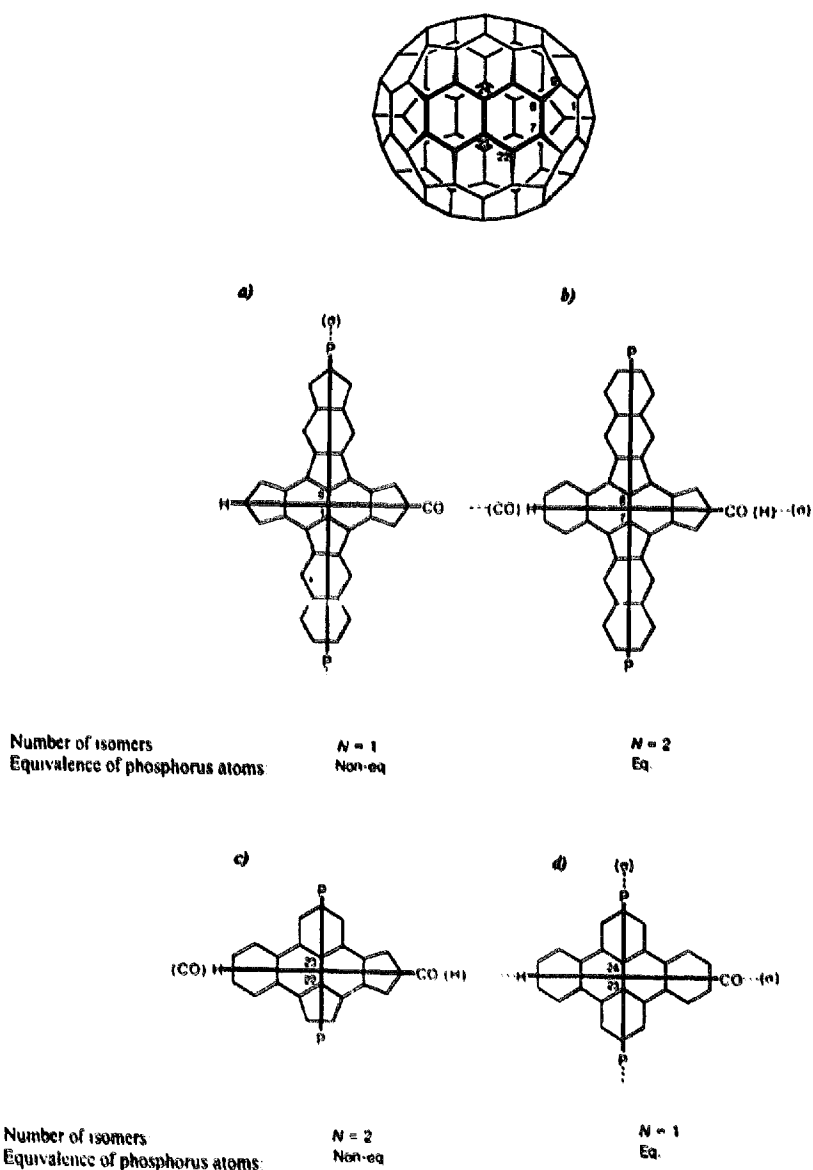


Fig. 3. The projection of a fragment of the  $\text{C}_{70}$  polyhedron along the  $\text{H-M-CO}$  and  $\text{P-M-P}$  bonds in complexes **5**, **6** showing the planes of symmetry ( $\sigma$ ), the number of possible geometric isomers ( $N$ ), and the equivalence of the phosphorus atoms in the cases where the metal is bonded to a fullerene moiety through (a) 1,9; (b) 7,8; (c) 22,23 or (d) 23,24 bonds.

i.e. at the 1,2 bond (for the numbering of the system see Ref. [32]). When addition of the metal atom involves the 1,9 bond of fullerene, the phosphorus atoms are equivalent (owing to the plane of symmetry which is perpendicular to this bond), and the complex itself should exist as a mixture of two geometrical isomers in the ratio 1:1 (in the first isomer, the hydride ligand is opposite a pentagon, and in the second one, the hydride ligand is opposite a hexagon; see Fig. 2(b)). This can be established by the  $^1\text{H}$  NMR spectrum which, in this case, should contain two triplets. When the metal atom adds to the 1,2 bond of fullerene, the phosphorus atoms will also be equivalent, while the complex will exist only as a single geometrical isomer (owing to the existence of two planes of symmetry, perpendicular and parallel to the 1,2 bond; see Fig. 2(a)). The same situation occurs in the case of complex 8. Where addition of the metallo-fragment involves the 1,9 bond of fullerene, the resultant complex itself should exist as a mixture of two geometrical isomers (Fig. 2(d)). When the metallo-fragment adds to the 1,2 bond, the complex should exist only as a single geometrical isomer (Fig. 2(c)). The presence of only one isomer, supported by

$^1\text{H}$  and  $^{31}\text{P}$  NMR spectra of the complexes 3, 4 and 8 unambiguously suggests that the fullerene is coordinated to the metal atom at the short bond along a 6–6 edge. It should be noted that these conclusions on the configuration and direction of coordination have been completely confirmed by X-ray data on compound 3 [18], prepared in the same manner by Balch et al.

In the case of complexes 5 and 6, the situation is dramatically complicated due to the fact that  $\text{C}_{70}$  already contains four non-equivalent reactive bonds (1,9; 7,8; 22,23; 23,24) along the 6–6 edges, which possess high bond orders (in this case the 1,9 and 7,8 bonds have very close values of bond order [32]). Moreover, there are four non-equivalent bonds along the 5–6 edges (1,2; 6,7; 7,22 and 21,22 bonds; for the numbering of the system see Ref. [32]). However, considerations of the symmetry and number of isomers formed make an unambiguous choice possible in this case also. The patterns in the  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra of the complexes indicate the presence of a single geometrical isomer with non-equivalent phosphorus atoms and correspond to coordination of the metal at the 1,9 bond (Fig. 3). Both iridium complexes of  $\text{C}_{70}$ , whose struc-

Table 1  
Analytical and spectroscopic data <sup>a</sup>

Compound	Yield (%)	UV/vis <sup>b</sup> (nm)	IR <sup>c</sup>		NMR $\delta$ <sup>d</sup> (ppm)
			$\nu_{\text{MH}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{CO}}$ ( $\text{cm}^{-1}$ )	
3 $\text{C}_{60}[\text{RhH}(\text{CO})(\text{PPh}_3)_2]$ C: 84.90 (84.60) H: 2.30 (2.27) P: 4.41 (4.50)	82–90	255(s), 327(s), 390(sh), 438(w), 618(w), 659(w)	2056	1984	$^1\text{H}$ : -9.38 (t, $^2J_{\text{PH}} = 9.5$ Hz, 1H, RhH); 7.3 (m, 30H, Ph) $^{31}\text{P}$ - $^1\text{H}$ $\delta$ : 39.7 (d, $^1J_{\text{RHP}} = 143$ Hz)
4 $\text{C}_{60}[\text{IrH}(\text{CO})(\text{PPh}_3)_2]$ C: 79.45 (79.28) H: 2.13 (2.19) P: 4.22 (3.99)	95	256( $1.15 \times 10^3$ ), 317( $4.8 \times 10^4$ ), 435( $1.0 \times 10^4$ ), 604( $4.4 \times 10^3$ ), 640( $3.6 \times 10^3$ )	2105	1988	$^1\text{H}$ : -9.16 (t, $^2J_{\text{PH}} = 17.4$ Hz, 1H, IrH); 7.5 (m, 30H, Ph) $^{31}\text{P}$ - $^1\text{H}$ $\delta$ : 7.8 (s)
5 $\text{C}_{70}[\text{RhH}(\text{CO})(\text{PPh}_3)_2]$ C: 84.78 (85.83) H: 1.87 (2.09) P: 3.66 (4.14)	60	332(s), 364(sh), 380(m), 464(m), 545(sh) <sup>e</sup>	2061 <sup>d</sup>	1981 <sup>d</sup>	$^1\text{H}$ : -10.23 (t, $^2J_{\text{PH}} = 10.0$ Hz, 1H, RhH); 7.3 (m, 30H, Ph) $^{31}\text{P}$ - $^1\text{H}$ $\delta$ : 40.7 (dd, $^1J_{\text{RHP}} = 142$ Hz, $^2J_{\text{PP}} = 30$ Hz) and 43.9 (dd, $^1J_{\text{RHP}} = 143$ Hz, $^2J_{\text{PP}} = 30$ Hz)
6 $\text{C}_{70}[\text{IrH}(\text{CO})(\text{PPh}_3)_2]$ C: 81.00 (81.92) H: 1.97 (2.15)	65	304(s), 372(m), 415(m), 441(m), 560(sh), 696(w)	2101 <sup>f</sup>	1986 <sup>f</sup>	$^1\text{H}$ $\delta$ : -10.16 (t, $^2J_{\text{PH}} = 17.5$ Hz, 1H, IrH); 7.5 (m, 30H, Ph) $^{31}\text{P}$ - $^1\text{H}$ $\delta$ : 4.6 (d, $^2J_{\text{PP}} = 36$ Hz) and 7.7 (d, $^2J_{\text{PP}} = 36$ Hz)
8 $\text{C}_{60}[\text{IrH}(\text{C}_8\text{H}_{12})$ ( $\text{PPh}_3$ ) $_2$ ] $\cdot 2\text{C}_6\text{H}_6$ C: 82.00 (81.71) H: 2.46 (2.80) P: 2.11 (2.15)	82.3	258(vs), 329(s), 436(m), 595(w), 636(sh)	2173	—	$^1\text{H}$ : -14.36 (d, $^2J_{\text{PH}} = 20.6$ Hz, 1H, IrH); 1.53, 1.72, 2.22, 2.44, 3.31, 3.92, 4.46, 5.14 and 5.49 (m, 12H, $\text{C}_8\text{H}_{12}$ ); 7.37 (s, 12H, $\text{C}_6\text{H}_6$ ); 7.42, 7.76 (m, 15H, Ph) $^{31}\text{P}$ - $^1\text{H}$ $\delta$ : 4.6 (s)

<sup>a</sup> Analytical data given as Found (Calc.) (%).

<sup>b</sup> In THF solution unless otherwise indicated.

<sup>c</sup> In KBr pellet unless otherwise indicated.

<sup>d</sup> In  $\text{CDCl}_3$  solution unless otherwise indicated.

<sup>e</sup> In toluene solution.

<sup>f</sup> In  $\text{C}_6\text{D}_6$  solution.

tures have been determined previously [14,17], have this geometry. It should be noted that these spectral patterns absolutely eliminate the possibility of the addition of the metal to any of the four non-equivalent bonds along the 5–6 edges of the C<sub>70</sub> fullerene, since if it took place the products obtained would always exist as mixtures of two geometrical isomers, as for coordination of the metal through a 5–6 edge of C<sub>60</sub> fullerene.

Thus, the organometallic hydrides of rhodium and iridium react with the fullerenes C<sub>60</sub> and C<sub>70</sub> with high regio- and stereoselectivity to form the exohedral complexes of  $\eta^2$ -type only.

### 3. Experimental details

UV and IR spectra were obtained on Specord M400 and M80 spectrometers respectively. <sup>1</sup>H NMR spectra at 400.3 MHz and <sup>31</sup>P-(<sup>1</sup>H) NMR spectra at 160.02 MHz were obtained on a Bruker AMX-400 spectrometer relative to TMS (internal standard) and 85% H<sub>3</sub>PO<sub>4</sub> (external standard) respectively. All experiments were carried out in an atmosphere of dry Ar, free of oxygen. The synthesis of complexes **4**, **6** and their deuterium analogs **9**, **10** has been described in a previous paper [27]. Analytical and spectroscopic data of complexes **3–6** and **8** are listed in Table 1.

#### 3.1. ( $\eta^2$ -C<sub>60</sub>)RhH(CO)(PPh<sub>3</sub>)<sub>2</sub> (**3**)

Complex **1** (102 mg, 0.111 mmol) in 5 ml of benzene was added with stirring to a suspension of C<sub>60</sub> (80 mg, 0.111 mmol) in 28 ml benzene. The violet reaction mixture immediately turned dark-green. After 5 min, 90 ml of ether (10 ml at a time) was added with stirring. The precipitate was filtered off, washed with ether and pentane and dried in vacuo. Microcrystalline dark-green powder (complex **3**, 125.9 mg, 82.4%) was obtained.

#### 3.2. ( $\eta^2$ -C<sub>70</sub>)RhH(CO)(PPh<sub>3</sub>)<sub>2</sub> (**5**)

Complex **1** (13.7 mg, 0.0149 mmol) in 0.5 ml of benzene was added with stirring to a suspension of C<sub>70</sub> (12.5 mg, 0.0149 mmol) in 4.5 ml of benzene. After 10 min, pentane (5 × 5 ml) was added with stirring. The resulting precipitate was filtered off, washed with pentane and dried in vacuo. A dark-brown (almost black) microcrystalline powder was obtained (complex **5**, 13.4 mg, 60%).

#### 3.3. ( $\eta^2$ -C<sub>60</sub>)IrH(C<sub>8</sub>H<sub>12</sub>)(PPh<sub>3</sub>)<sub>2</sub> · 2C<sub>6</sub>H<sub>6</sub> (**8**)

Complex **7** (57.3 mg, 0.0694 mmol) in 4 ml of benzene was added with stirring to a solution of C<sub>60</sub> (50 mg, 0.0694 mmol) in 50 ml of benzene. The reaction mixture was stirred for 12 h, then methanol (50 ml) and

hexane (20 ml) were sequentially added. After 2 h, the resulting precipitate was filtered off, washed with methanol (2 × 5 ml) and hexane (2 × 5 ml) and dried in vacuo. The complex **8** (82.3 mg, 82.3%) was obtained as a black–green powder.

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