

Organometallic hydrides as reactants in fullerene chemistry. Interaction of C₆₀ and C₇₀ fullerenes with HIr(CO)(PPh₃)₃

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The iridium hydride complex HIr(CO)(PPh₃)₃ reacts with fullerenes C₆₀ and C₇₀ yielding (η²-C_n)IrH(CO)(PPh₃)₂ (n = 60, 70) complexes. Their composition, configuration, and the position of the double bond coordinated with the metal atom in the fullerene moiety have been established by IR studies (comparison with deuterated analogs), and ¹H and ³¹P NMR spectroscopy.

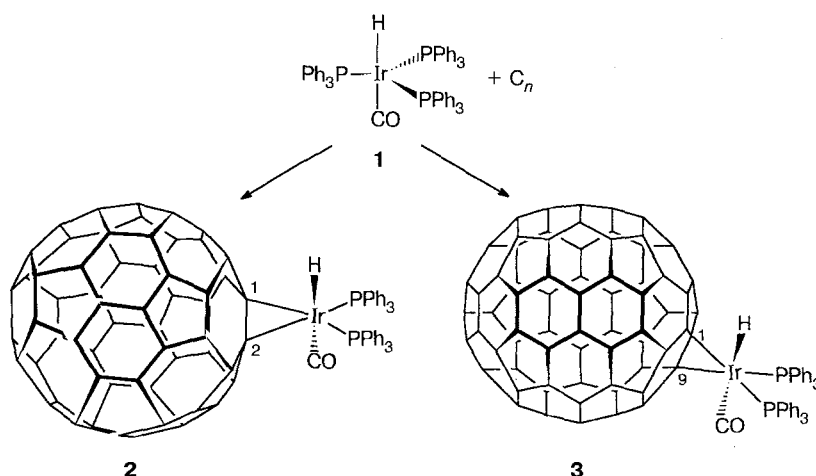
Key words: fullerene, iridium hydride complexes; configuration of complexes; coordination; regioselectivity.

The investigation of the reactivity of fullerenes towards various organometallic complexes provides important information on the structure and chemical behavior of polyene electron-acceptor molecules such as fullerenes C₆₀ and C₇₀.¹⁻¹⁹ Recently, the use of transition metal hydrides as reactants in the chemistry of fullerenes has been reported.^{15,18,19} A distinguishing feature of these reactants, as compared with organometallic compounds studied so far, is that they can react with fullerenes in two essentially different ways: (i) by direct coordination of the metal atom at the double bonds; (ii) by the addition of a M-H bond to the fullerene polyene system. The interaction of C₆₀ and C₇₀ with HRh(CO)(PPh₃)₃^{15,19} exemplifies the first reaction pathway, while functionalization of a C₆₀ molecule via

the intermediate formation of the hydrozirconation product¹⁸ is an example of the second route. In addition, when the reaction proceeds according to the first pathway, the presence of a hydride ligand in the complexes formed makes it possible to readily determine both their configuration and the bond in the fullerene cages involved in coordination of the metal. This has been exemplified by us for (η²-C_n)RhH(CO)(PPh₃)₂ (n = 60, 70) complexes¹⁹ and is summarized in the present paper, in which the results of our study of the interaction of C₆₀ and C₇₀ fullerenes with HIr(CO)(PPh₃)₃ (**1**) are presented.

When a yellow solution of **1** in benzene or toluene is added to an equimolar amount of a violet solution of C₆₀ in the same solvent, a green solution is immediately

Scheme 1



produced and a dark-green $(\eta^2\text{-C}_{60})\text{IrH}(\text{CO})(\text{PPh}_3)_2$ complex (**2**) can be precipitated from this solution with pentane or methanol in 90–95 % yield (Scheme 1). The electronic spectrum of the reaction mixture in toluene recorded immediately after mixing of the reagents differs essentially in the visible region from that of the initial C_{60} , and contains three bands at 432, 600, and 635 nm of much higher intensity. It should be noted that the reaction is completed in 15–20 min. The dark-brown (almost black) $(\eta^2\text{-C}_{70})\text{IrH}(\text{CO})(\text{PPh}_3)_2$ complex (**3**) can be obtained in the same way in 65 % yield (see Scheme 1).

The configuration of complexes **2** and **3** was determined from IR and NMR spectroscopic data. The IR spectra (KBr pellets)* of these compounds contain strong νCO bands at 1988 cm^{-1} (**2**) and 1989 cm^{-1} (**3**), as well as weak νIrH bands at 2105 cm^{-1} (**2**) and 2130 cm^{-1} (**3**). The shift of the νCO band observed in the spectra of **2** and **3** as compared with that of the starting complex **1** (1920 cm^{-1} , Nujol mull) is due to the strong electron-acceptor nature of the η^2 -coordinated fullerene molecule.^{10–15,19} Unlike analogous rhodium complexes $(\eta^2\text{-C}_n)\text{RhH}(\text{CO})(\text{PPh}_3)_2$, whose IR spectra exhibit "equalizing" of the intensities of the νCO and νRhH bands¹⁹ due to the resonance coupling between these two vibrations, no effect of this kind arises in the spectra of **2** and **3** due to the greater difference between the frequencies of the vibra-

tions. Therefore, the isostructural deuterium complexes $(\eta^2\text{-C}_n)\text{IrD}(\text{CO})(\text{PPh}_3)_2$, **4** ($n = 60$) and **5** ($n = 70$), were prepared in the same manner to determine the coordination configuration of the central iridium atom. The νCO band is observed in the IR spectra at 2009 cm^{-1} (**4**) and at 2011 cm^{-1} (**5**), *i.e.*, it is shifted by $21\text{--}22\text{ cm}^{-1}$. The observed shift and its magnitude attest to $\nu\text{IrH}\text{--}\nu\text{CO}$ coupling, which is possible when both ligands are in the *trans*-position relative to each other.^{20,21} This fact completely determines the overall configuration of complexes **2** and **3**.

The results obtained are in good agreement with NMR data. The ^1H NMR spectra (in C_6D_6) of both complexes contain a triplet at $\delta -8.83$ ($^2J_{\text{H,P}} = 18.0\text{ Hz}$) (**2**)* and at $\delta -10.16$ ($^2J_{\text{H,P}} = 17.7\text{ Hz}$) (**3**) which is assigned to the hydride proton. A complex multiplet is observed in the spectra of both compounds at $\sim 7.5\text{ ppm}$, which is assigned to phenyl protons. The observed multiplicity and the magnitude of the $^2J_{\text{H,P}}$ spin-coupling constant attest to the fact that the two phosphine ligands in **2** and **3** are in the *cis*-position relative to the hydride proton.²² The $^{31}\text{P}\text{--}\{^1\text{H}\}$ NMR spectrum of **2** contains a singlet at 7.8 ppm , which corresponds to a single isomer with equivalent phosphorus atoms. In the case of **3**, an AB quartet is observed in the spectrum, $\delta\text{P}(1)\ 4.6$ and $\delta\text{P}(2)\ 7.7$, which corresponds to two non-equivalent phosphorus atoms in a *cis*-position relative to each other; this is also confirmed by the value of the $^2J_{\text{P}(1),\text{P}(2)}$

* Similar values are also observed in solutions of C_6D_6 (see Experimental).

* Also observed in CDCl_3 : $\delta -9.16$, $^2J_{\text{H,P}} = 17.4\text{ Hz}$.

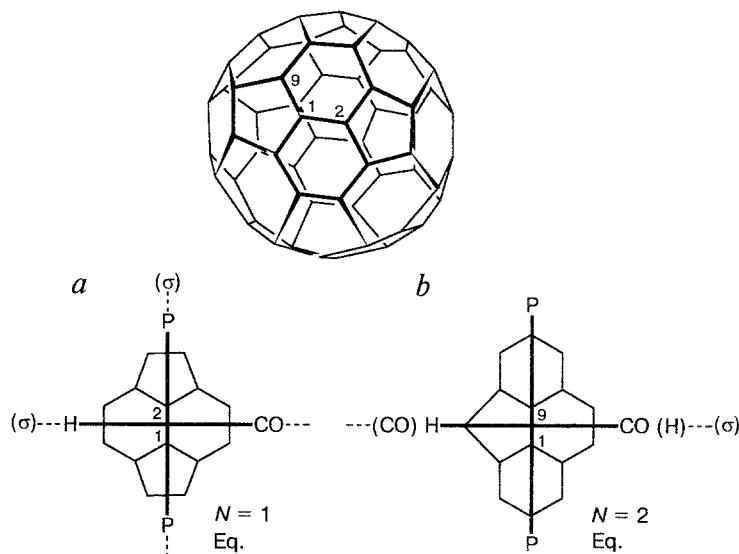


Fig. 1. The projection of fragment of the C_{60} polyhedron along the H--Ir--CO and P--Ir--P bonds showing the planes of symmetry (σ), the number of possible geometric isomers (N), and the equivalence of the phosphorus atoms (Eq.) when the Ir atom is bonded to fullerene through a 1,2 bond (a) or through a 1,9 bond (b).

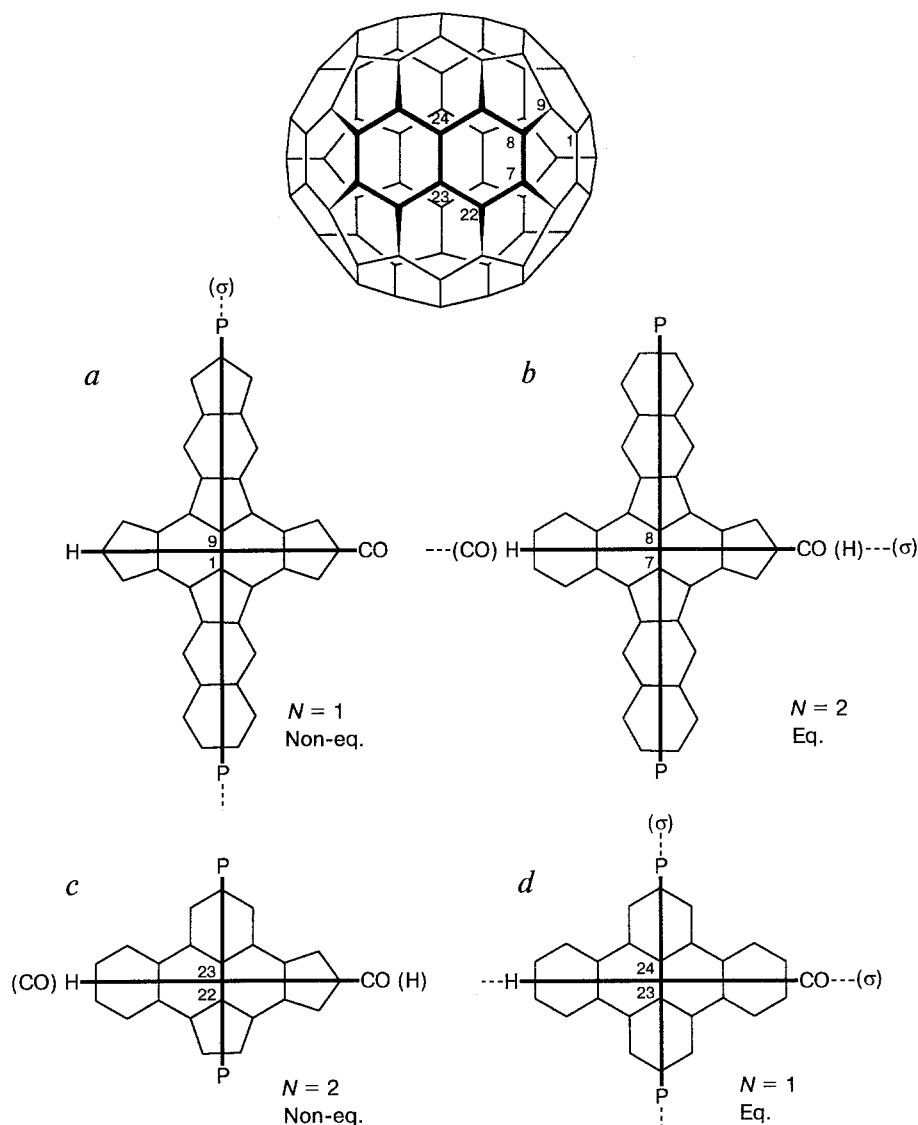


Fig. 2. The projection of fragment of the C_{70} polyhedron along the H—Ir—CO and P—Ir—P bonds showing the planes of symmetry (σ), the number of possible geometric isomers (N), and the equivalence of phosphorus atoms (Eq.) when the Ir atom is bonded to fullerene through 1,9 (a); 7,8 (b); 22,23 (c) or 23,24 (d) bonds.

coupling constant ($^2J_{P(1),P(2)} = 36 \text{ Hz}$).²² Thus, the configuration of iridium complexes **2** and **3** coincides with that of their rhodium analogs, moreover, the structure of the $(\eta^2-C_{60})RhH(CO)(PPh_3)_2$ complex was independently established by X-ray diffraction analysis.¹⁵

The inherent configuration of complexes **2** and **3** (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 reasoning from the combined data of 1H and ^{31}P NMR spectroscopy and the number of possible isomers and their symmetry. Thus, in complex **2** fullerene C_{60} may be coordinated with the iridium atom either through a 5—6 edge, *i.e.*, at the 1,9 bond, or

through a 6—6 edge, *i.e.*, at the 1,2 bond (for the numbering of the system see Ref. 23). When addition of the iridium 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 will 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. 1). This can be readily established by the 1H NMR spectrum which, in this case, should contain two triplets. When the iridium 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. 1). The ^1H and ^{31}P NMR spectra of **2** (see above) are in complete agreement with the latter case and confirm the well known fact previously established from X-ray data for different fullerene complexes⁸⁻¹⁶ that the 1,2 bond is more reactive than the 1,9 bond.²³

In the case of $(\eta^2\text{-C}_{70})\text{MH}(\text{CO})(\text{PPh}_3)_2$ complexes, where $\text{M} = \text{Rh}^{19}$ and Ir (**3**), the situation is dramatically complicated due to the fact that C_{70} already contains four nonequivalent reactive bonds (1,9; 7,8; 22,23; 23,24) along the 6—6 edges, which possess high bond order. Moreover, the 1,9 and 7,8 bonds possess close values of bond order.²³ However, the consideration of the symmetry and the number of isomers formed makes an unambiguous choice possible in this case as well. The pattern of the ^1H and ^{31}P NMR spectra of the complexes under consideration, which indicate the presence of a single geometrical isomer with nonequivalent phosphorus atoms, corresponds to coordination of the metal at the 1,9 bond* (Fig. 2), as is the case for both Ir complexes of C_{70} whose structures have been determined previously.^{11,14}

Thus, organometallic hydrides of the $\text{HM}(\text{CO})(\text{PPh}_3)_3$ type ($\text{M} = \text{Rh}$ and Ir) exhibit high regio- and stereoselectivity in reactions with the C_{60} and C_{70} fullerenes. This was determined by means of IR and NMR spectroscopy due to the presence of a hydride ligand in the η^2 -type complexes formed. These properties of organometallic hydrides and the high stability of the products obtained may be useful in studies of higher fullerenes.

Experimental

UV and IR spectra were obtained on Specord M400 and Specord M80 spectrometers, respectively. ^1H NMR spectra at 200.13 MHz and ^{31}P - $\{^1\text{H}\}$ NMR spectra at 80.01 MHz were obtained on a Bruker WP-200-SY spectrometer relative to TMS (internal standard) and 85 % H_3PO_4 (external standard), respectively. All experiments were carried in an atmosphere of dry Ar free of oxygen.

$(\eta^2\text{-C}_{60})\text{IrH}(\text{CO})(\text{PPh}_3)_2$ (2**).** Complex **1** (80 mg, 0.079 mmol) in 4 mL of benzene was added with stirring to a solution of C_{60} (60 mg, 0.083 mmol) in 15 mL of benzene, and the violet reaction mixture became dark-green. After 30 min, pentane (24 mL) and methanol (60 mL) were sequentially added to the reaction mixture and left overnight. The precipitate was filtered off, washed with methanol and

pentane, and dried *in vacuo*. A microcrystalline dark-green powder (complex **2**, 100 mg, 95 %) was obtained.* Found (%): C, 79.45; H, 2.13; P, 4.22. $\text{C}_{97}\text{H}_{31}\text{OP}_2\text{Ir}$. Calculated (%): C, 79.28; H, 2.19; P, 3.99. UV (THF), $\lambda_{\text{max}}/\text{nm}$ (ϵ): 256 ($1.15 \cdot 10^5$); 317 ($4.8 \cdot 10^4$); 435 ($1.0 \cdot 10^4$); 604 ($0.44 \cdot 10^4$); 640 ($0.36 \cdot 10^4$). IR (C_6D_6), ν/cm^{-1} : 2106 (IrH); 1985 (CO). ^1H NMR (C_6D_6), δ : -8.83 (t, 1 H, IrH , $^2J_{\text{H,P}} = 18.0$ Hz); 7.5 (m, 30 H, Ph). ^{31}P - $\{^1\text{H}\}$ NMR (C_6D_6), δ : 7.8 (s).

$(\eta^2\text{-C}_{70})\text{IrH}(\text{CO})(\text{PPh}_3)_2$ (3**).** Complex **3** was obtained in the same manner from complex **1** (4.4 mg, 0.0043 mmol) in 0.5 mL benzene and C_{70} (4.0 mg, 0.00475 mmol) in 1.5 mL of benzene. After 1 mL of methanol has been added, complex **3** (4.5 mg, 65 %) precipitated as a dark-brown microcrystalline powder. Found (%): C, 81.00; H, 1.97. $\text{C}_{107}\text{H}_{31}\text{OP}_2\text{Ir}$. Calculated (%): C, 81.92; H, 2.15. UV (THF), $\lambda_{\text{max}}/\text{nm}$: 304 (s), 372 (m), 415 (m), 441 (m), 560 (sh), 696 (w). IR (C_6D_6), ν/cm^{-1} : 2101 (IrH); 1986 (CO). ^1H NMR (C_6D_6), δ : -10.16 (t, 1 H, IrH , $^2J_{\text{H,P}} = 17.5$ Hz); 7.5 (m, 30 H, Ph). ^{31}P - $\{^1\text{H}\}$ NMR (C_6D_6), δ : 4.6 and 7.7 (AB system, $^2J_{\text{P,P}} = 36$ Hz).

$(\eta^2\text{-C}_{60})\text{IrD}(\text{CO})(\text{PPh}_3)_2$ (4**).** Similarly to complex **2**, complex **4** was obtained from C_{60} (7.5 mg, 0.0104 mmol) in 8 mL of benzene and $\text{DIr}(\text{CO})(\text{PPh}_3)_3$ **21** (10.0 mg, 0.0099 mmol) in 1.5 mL of benzene in an atmosphere of D_2 . Hexane (30 mL) and methanol (20 mL) were sequentially added to the reaction mixture to give after 30 min (9.0 mg, 62 %) of complex **4** as a dark-green microcrystalline powder. IR (KBr), ν/cm^{-1} : 2009 (CO).

$(\eta^2\text{-C}_{70})\text{IrD}(\text{CO})(\text{PPh}_3)_2$ (5**).** Similarly to complex **4**, complex **5** was obtained from C_{70} (1.0 mg, 0.00119 mmol) in 1 mL of benzene and $\text{DIr}(\text{CO})(\text{PPh}_3)_3$ **21** (1.15 mg, 0.00114 mmol) in 0.5 mL of benzene in an atmosphere of D_2 . Complex **5** (1.08 mg, 60 %) was obtained as a dark-brown microcrystalline powder after precipitation with methanol. IR (KBr), ν/cm^{-1} : 2011 (CO).

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* It should be noted that the ^1H and ^{31}P NMR spectral patterns observed absolutely eliminate the possibility of the addition of metal to any one of the four non-equivalent bonds (1,2; 6,7; 7,22; and 21,22) arranged on a 5—6 edge of the C_{70} fullerene polyhedron, since if this were the case the adducts would always exist as mixtures of two geometrical isomers, like for coordination of the metal through 5—6 edge of C_{60} fullerene.

* Complex **2** was obtained in 73 % yield after precipitation with pentane and subsequent stirring for 30 min.

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