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Optically active rhodium and iridium C_{60} complexes containing the enantiomeric ligand (+)DIOP: (η^2-C_{60})MH(CO)[(+)DIOP] (M = Rh, Ir)

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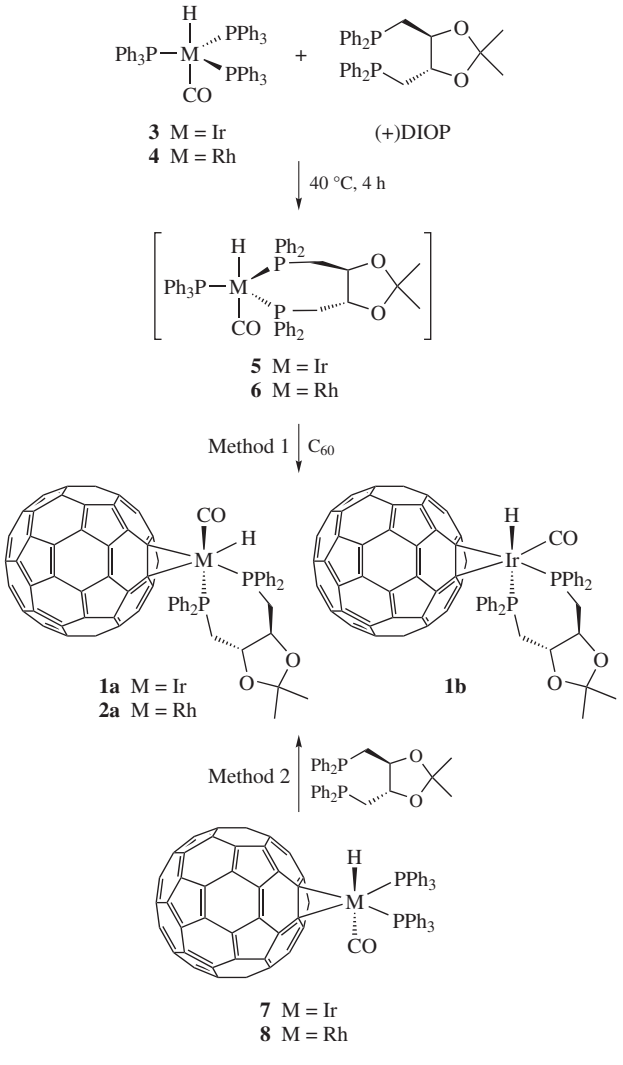
The fullerene–metal complexes (η^2-C_{60})MH(CO)[(+)DIOP] (M = Ir, Rh) have been prepared by the exchange reaction of PPh_3 in corresponding (η^2-C_{60})MH(CO)(PPh_3)$_2$ for the chelate optically active ligand (+)DIOP [(+)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)ethane] and their structures assigned.

Fullerenes can form complexes with the η^2-coordination of platinum group metals.[1,2] However, a few fullerene–metal complexes bearing enantiomeric ligands have been reported,[3–6] although such compounds are of interest for asymmetric catalysis. Metallofullerene complexes, in particular (η^2-C_{60})IrH(CO)[(+)DIOP], are potential efficient components of organic solar photoelements.[7]

Here, we report the synthesis, structural assignment and circular dichroism of iridium and rhodium C_{60} complexes (η^2-C_{60})-MH(CO)[(+)DIOP] (**1**, **2**) having the optically active diphosphine ligand (+)DIOP [(+)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis-(diphenylphosphino)ethane]. Using IR and multinuclear NMR spectroscopy, we found that **1** can exist as a mixture of two geometrical isomers, whereas **2** occurs as only one isomer.

The synthesis of complexes **1** and **2** was performed in two ways. The first includes a two-step procedure (Scheme 1, method 1),[†] which started with the exchange of two PPh_3 ligands in the nonfullerene complex $HM(CO)(PPh_3)_3$ (**3**, **4**) for (+)DIOP to afford {HM(CO)[(+)DIOP](PPh_3)} (**5**, **6**). Fullerene was introduced at the second step, when **5** or **6** reacted (without isolation) with C_{60} at 60 °C to give **1** or **2**, respectively.



Scheme 1

Complex **1** was formed as a mixture of isomers **1a** and **1b**. TLC demonstrated that, initially (during ~0.5 h), isomer **1b** was the major product. In the course of reaction, the ratio between isomers changed, and only isomer **1a** was present after 5 h. A similar situation was observed at a lower temperature at the

[†] The NMR spectra were recorded on a Bruker AMX-400 instrument. Chemical shifts in ^{1}H NMR spectra are given relative to the residual signals of C_6D_6 (7.23 ppm) (internal standard) recalculated to TMS; in ^{31}P spectra, relative to H_3PO_4 (85%) as an external standard. The IR and UV spectra were obtained on a Specord M80 and Shimadzu UV2501PC instruments, respectively.

The syntheses were carried out in dry purified argon and dry and purified solvents using the Schlenk tubes.

Synthesis of complex (η^2-C_{60})IrH(CO)[(+)DIOP] **1a**,**b**. *Method 1.*

First step. (+)DIOP (10 mg, 0.02 mmol) was added with stirring to 20 mg (0.02 mmol) $IrH(CO)(PPh_3)_3$ **3** in 5 ml of benzene. The solution was heated at 40 °C for 4 h. *Second step.* The solution obtained at the first step was treated with 15 mg (0.021 mmol) of C_{60} in benzene (15 ml) and stirred for 5 h at 60 °C, evaporated to 1/3 and 50 ml of pentane was added. The precipitate formed was filtered off, washed with pentane and dried *in vacuo*. Then, it was chromatographed on a SiO_2 column (d = 1.3 cm, h = 30 cm) being eluted subsequently with hexane (to remove excess C_{60}) and benzene–hexane (4:1). Thus prepared dark-green solution was evaporated to 1/3 by volume; pentane (10-fold volume) was added and left for 2 h at 4 °C. The precipitate was separated, washed with pentane and dried *in vacuo* to afford 14.6 mg (52%) of **1a** as dark-green powder.

When the second step was performed at 40 °C for 7 h, 9.0 mg (32%) of **1a** and 5.4 mg (19%) of **1b** were isolated after column chromatography.

IR (KBr, ν/cm^{-1}): 2088 (Ir–H), 1979 (CO). UV (toluene, λ_{max}/nm): 311, 345, 440. ^{1}H NMR (C_6D_6) δ: 0.44 (dd, 1H, H-Ir $^2J_{HP^1}$ 17 Hz, $^2J_{HP^2}$ 21 Hz). ^{31}P{^{1}H} NMR (C_6D_6) δ: 10.16, –12.30 (AB system, $^2J_{P^1P^2}$ 46 Hz). Found (%): C, 77.09; H, 2.86; P, 3.96. Calc. for $C_{77}H_{21}IrO_3P_2$ (%): C, 76.71; H, 2.31; P, 4.30.

second step (40 and 30 °C instead of 60 °C), but reaction occurred more slowly to complete in 7 or 8 h, respectively. At lower temperature, the stability of **1b** increased substantially. For instance, **1b** was the only isomer at 40 °C after 3 h. We suppose that this observation points that **1b** is the kinetically controlled product, whereas **1a** is thermodynamically controlled. This is supported by the fact that isomer **1b** converts completely into **1a** in benzene at 60 °C for 1 h. Moreover, analytically pure crystalline isomer **1b** after a week at room temperature converts into **1a** by 50% in a solid state.

The second method (Scheme 1, method 2)‡ consists in the exchange reaction of two PPh_3 ligands in the fullerene complex (η^2-C_{60})MH(CO)(PPh_3)$_2$ (**7**, **8**) for the chelate ligand (+)DIOP.

In this case, a mixture of isomers **1a** and **1b** was also formed. After 1 h, the amount of **1b** was greater than that of **1a**, but **1a** dominated after 2 h. Near completion of the reaction (~8 h), the fraction of **1b** gradually decreased. Note that the ligand exchange did not come to the end even after 16 h and the use of a 20-fold excess of (+)DIOP. This may be due to the reversibility of reaction and the presence of PPh_3 in the reaction mixture.

For the rhodium complex, all reactions occur smoothly and rapidly at room temperature. This is probably owing to the easier dissociation of the Rh–C_{60} bond in comparison with that of the Ir–C_{60} bond, as observed previously for **7** and **8**.[8,9] Both of the synthetic ways lead to single stable isomer **2a**.

The structures of the complexes have been determined on the basis of ^{1}H and ^{31}P{^{1}H} NMR spectra. The complexes (η^2-C_{60})MH(CO)(PPh_3)$_2$, where M = Ir, Rh,[8–11] have the structures wherein the equatorial plane is formed by two C and two P atoms, whereas CO and H occupy the axial positions. A change of triphenylphosphine for DIOP causes the disappearance of the *trans*-isomers, which could be more advantageous on pure steric grounds because the bulkier DIOP ligands would be far from fullerene. On the contrary, two *cis*-isomers **1a** and **2a** were formed for the iridium addend and one *cis*-isomer **1b**, which is thermodynamically more stable in the case of rhodium. This follows unambiguously from NMR spectra showing two nonequivalent phosphorus atoms in the DIOP compounds. This finding can be explained only by the attractive interaction between the phenyl group at phosphorus and the fullerene moiety.

In ^{1}H NMR spectra the most informative signals are due to the hydride atom. For complexes **1a** and **2a**, the multiplicity and values of the spin–spin hyperfine splitting constants give evidence that H is in the *cis*-position to both P atoms of (+)DIOP, whereas one P and CO group are situated in the *trans*-position.

For complex **1b**, the ^{1}H NMR spectrum exhibits a doublet of doublets at –10.32 ppm; the chemical shift is characteristic of hydride H at Ir with the spin–spin coupling constants $^2J_{HP^1}$ 17 Hz and $^2J_{HP^2}$ 143 Hz. It was shown using the selective decoupling of ^{31}P that the hydride H is situated in *cis*-position to one P ($^2J_{HP^1}$ 17 Hz) and in the *trans*-position to another P atom ($^2J_{HP^2}$ 143 Hz).

It was interesting to monitor at which preparation stage (Scheme 1, method 1) the P atoms of (+)DIOP became nonequivalent. In this connection, complexes **1**, **3** and **5** were studied by ^{1}H, ^{1}H{^{31}P} and ^{31}P{^{1}H} NMR spectroscopy. After the addition of (+)DIOP, **3** completely converted into **5**. In the ^{31}P{^{1}H} spectrum, four signals were observed: 16.4 ppm (PPh_3 coord.), two signals of 2P atoms of the coordinated (+)DIOP at –7.39 (s) and 7.9 (s) ppm, and –4.7 (s) ppm (free PPh_3). Multiplicity, chemical shifts, and relative intensities show that in complex **5** all three P atoms are coordinated to iridium and placed in equatorial positions. This means that the formation of two isomers proceeds at the stage of formation of **1** rather than **5**.

Investigation of rhodium complex **2a** showed that, after the addition of (+)DIOP to **4** (Scheme 1, method 1), the following signals were observed in the ^{31}P{^{1}H} NMR spectrum: a singlet of free PPh_3 at –4.7 ppm, two triplets at 22.0 ($^2J_{PP}$ 94 Hz) and 21.1 ($^2J_{PP}$ 84 Hz) ppm owing to 2P atoms of (+)DIOP and a doublet at 17.0 ppm due to splitting on ^{103}Rh. In the ^{1}H NMR spectrum, a multiplet was observed, which became a singlet at –9.6 ppm corresponding to the hydride H in the ^{1}H{^{31}P} regime. This points that the exchange of two PPh_3 for (+)DIOP in **4** gives HRh(CO)(PPh_3)[(+)DIOP] **6**, which probably has a geometry of trigonal bipyramid.

Like in previous studies of optically active fullerene derivatives,[4,12,13] the CD spectra§ of (+)DIOP η^2-C_{60} fullerene complexes of iridium (**1a** and **1b**) and rhodium (**2a**) (Figure 1) exhibit many Cotton effects (CEs) which can be only tentatively attributed to the intrinsic electron transitions in the C_{60} core itself or to electron density transfer from the metal–ligand fragment to the fullerene core. Nonetheless, the long-waved CE (above ~575 nm)

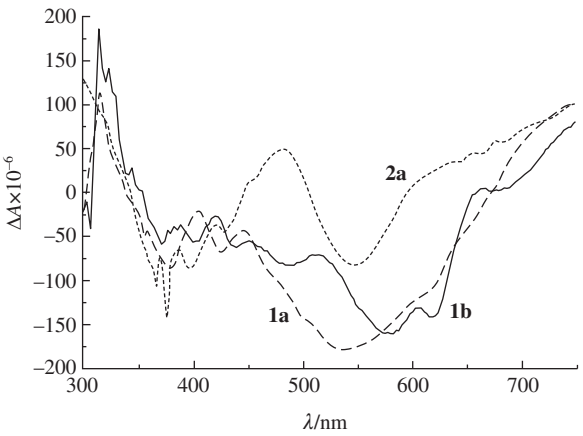


Figure 1 CD spectra of the complexes (η^2-C_{60})Ir(CO)[(+)DIOP] **1a**,**b** and (η^2-C_{60})Rh(CO)[(+)DIOP] **2a**.

Synthesis of complex (η^2-C_{60})RhH(CO)[(+)DIOP] **2a**. *Method 1*.

First step. (+)DIOP (6 mg, 0.012 mmol) was added to 10 mg (0.011 mmol) of RhH(CO)(PPh_3)$_3$ **4** in 5 ml of benzene. The solution was stirred for 1.5 h. *Second step*. The solution obtained was treated with 8 mg (0.011 mmol) of C_{60} in benzene (15 ml) and stirred for 0.5 h at room temperature, evaporated to 1/3 and 50 ml of pentane was added. The precipitate formed was filtered off, washed with pentane and dried. Purification was done as in method 1 for complex **1**. Yield, 4.0 mg (27%) of **2a**. IR (KBr, ν/cm^{-1}): 2051 (Rh–H), 1986 (CO). UV-VIS (toluene, λ_{max}/ nm): 332 (s), 440 (m). ^{1}H NMR (C_6D_6) δ: 9.40, 9.70 (dd, 1H, HRh, $^2J_{HP}$ 9 Hz). ^{31}P{^{1}H} NMR, δ: 22.56 (dd $^1J_{Rh–P}$ 135 Hz, $^2J_{PP}$ 45 Hz), 24.12 (dd, $^1J_{Rh–P}$ 137 Hz, $^2J_{PP}$ 45 Hz). Found (%): C, 81.97; H, 2.73; P, 3.99. Calc. for $C_{77}H_{21}RhO_3P_2$ (%): C, 81.78; H, 2.46; P, 4.58.

‡ *Synthesis of complex (η^2-C_{60})IrH(CO)[(+)DIOP]* **1a**,**b**. *Method 2*.

(+)DIOP (25.4 mg, 0.051 mmol) was added with stirring to 73.3 mg (0.050 mmol) of (η^2-C_{60})IrH(CO)(PPh_3)$_2$ **7** in benzene (20 ml). After 8 h at 60 °C the dark-green solution was concentrated to 1/3 *in vacuo*; 50 ml of pentane was added and left for 2 h. The precipitate formed was filtered off, washed with pentane and dried. Purification was performed as in method 1. Yield, 50 mg (70%) of **1a** as dark-green powder.

Synthesis of complex (η^2-C_{60})RhH(CO)[(+)DIOP] **2a**. *Method 2*.

(+)DIOP (4.0 mg, 7.99 μmol) was added with stirring to 10 mg (7.26 μmol) of (η^2-C_{60})RhH(CO)(PPh_3)$_2$ **8** in 5 ml of benzene. After 0.5 h, a dark-green solution was concentrated to 1/3 and 50 ml of pentane was added. The precipitate formed was filtered off, washed with pentane and dried *in vacuo*. The further purification was carried out using chromatography on a SiO_2 plate with benzene–hexane (4:1) as an eluent. The product was extracted with benzene, the extract was concentrated to 1/3, and a 10-fold excess of pentane was added to give 5.0 mg (51%) of **2a** as dark-green powder.

§ The CD spectra of **1a**,**b** and **2a** were recorded using a SCD-2 dichrograph (Institute of Molecular Biology and Institute of Spectroscopy, Russian Academy of Sciences) in the range of 300–800 nm at 23 °C in 1 cm or 0.5 cm quartz cells.

corresponds definitely to the electron transitions within C_{60}, whereas those in the shorter wavelengths region may reflect the electronic interaction between the core and addends. As can be seen in Figure 1, the positions of CEs for the iridium (**1a**) and rhodium (**2a**) complexes are similar (535, 537 nm). This, in combination with the NMR data, allowed us to confirm the similar geometries; the CD spectrum of **1b** isomer exhibits two shifted CEs (582, 607 nm), which evidences the different placement of ligands within the octahedral arrangement.

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