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ESR study of radical adducts of dialkoxyphosphoryl radicals with $(\eta^2\text{-}C_{60})IrH(CO)(PPh_3)_2$ and $(\eta^2\text{-}C_{60})IrH(C_8H_{12})(PPh_3)$

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The reaction of phosphoryl radicals with $(\eta^2\text{-}C_{60})IrH(CO)(PPh_3)_2$ and $(\eta^2\text{-}C_{60})IrH(C_8H_{12})(PPh_3)$ was shown (ESR) to result in the formation of isomers differing in the constants of hyperfine interaction (HFI) with ^{31}P nuclei, *g*-factors, and linewidths. It is likely that the addition of phosphoryl radicals at a distance of two-three bond lengths from the metallofragment is predominant.

Key words: ESR, phosphoryl radical, fullerenyl radical, metallocomplex, isomers.

Insertion of metallocomplexes or a methylene fragment in fullerenes causes a drastic decrease in the polyhedron symmetry and the appearance of several groups of nonequivalent carbon atoms. Distortion of the fullerene polyhedron occurs simultaneously. In this connection, there arises a question of the effect of different groups bonded to fullerene C_{60} on the reactivity of the atoms of the distorted fullerene sphere.

It was shown previously[1] that the addition of dialkylphosphoryl radicals to metallocomplexes $C_{60}M(PPh_3)_2$ (M = Pt, Pd) results in the formation of at least five isomers that differ in the constants of hyperfine interaction (HFI) with the nucleus of the phosphorus atom of the phosphoryl residue and *g*-factors. However, these data did not make it possible to decide which of the isomers corresponded to the addition of the phosphoryl radical in the vicinity of the metal atom. In studies of reactions of the phosphoryl radicals with $C_{60}C(C_6H_4OMe)_2$, the most stable of the seven isomers formed was shown to result from the addition of the phosphoryl radical in the vicinity of the methylene group.[2]

In this work, the ESR spectra of radical adducts of the phosphoryl radicals with the octahedral hydride

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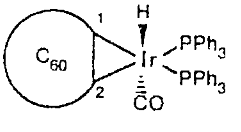
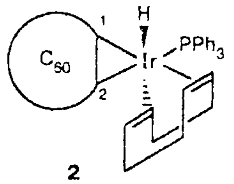
metallocomplexes of fullerene, $(C_{60})IrH(CO)(PPh_3)_2$ (**1**) and $(C_{60})IrH(C_8H_{12})(PPh_3)$ (**2**), were studied.



1



2

Experimental

Compounds **1** and **2** were obtained according to the known procedure.[3,4] A DRSh-1000 high-pressure mercury lamp was used for the photochemical generation of radicals. The solutions under study were irradiated by filtered (620—680 nm) or nonfiltered light. The ESR spectra were recorded on a Varian E-12A spectrometer.

Results and Discussion

Phosphoryl radicals were generated according to the described procedure[1,2] by photolysis of a diphosphorylmercury compound in a saturated toluene solution of **1** or **2** (Scheme 1).

Scheme 1

$$Hg[P(O)(OPr^i)_2]_2 \xrightarrow{h\nu} 2\,{}^{\bullet}P(O)(OPr^i)_2 + Hg$$

$$(C_{60})IrH(CO)(PPh_3)_2 + {}^{\bullet}P(O)(OPr^i)_2 \longrightarrow$$

$$\longrightarrow (Pr^iO)_2(O)P{-}^{\bullet}(C_{60})IrH(CO)(PPh_3)_2$$

The ESR spectra of radical adducts of the phosphoryl radicals with metallocomplex **1** (**3**—**6**) recorded with an interval of 8 min are shown in Fig. 1, *a*—*c*.

The overlap of the ESR spectra of several isomers (**3**—**6**) differing in their *g*-factors and HFI constants complicates the unambiguous determination of their magnetic-resonance parameters. However, accounting for the differences in the linewidths and intensities of individual isomers allowed us to determine these parameters: **3**, a_P = 66.7 G, g = 2.0026; **4**, a_P = 64.25 G, g = 2.0037; **5**, a_P = 63.5 G, g = 2.0023; **6**, a_P = 59.25 G, g = 2.0027. Spectral parameters of adduct **5** coincide with those of ${}^{\bullet}C_{60}P(O)(OPr^i)_2$,[5] which points to partial demetalation of the complex under the reaction conditions. However, the adducts of the Ir hydride complex are more stable under photolysis conditions as compared to the radical adducts of the phosphoryl radicals with the platinum or palladium metallocomplexes of fullerene, and accumulation of the demetalated radical proceeds 5—10 times slower. This is likely associated with a stronger bond between Ir and fullerene. The width of the spectral line of isomer **3** (2.5 G) is 2.5 times larger than those of other isomers (~1 G), and the intensity of its ESR spectrum exceeds the overall intensity of the spectra of other metal-containing phosphorylfullerenyl radicals by a factor of ~4. An increase in the linewidth of isomer **3** can be due to the HFI of the unpaired electron with the nuclei of the Ir, H, and P (of triphenylphosphine) atoms as well as with the proton, *i.e.*, it can be assumed that the phosphoryl radical is in a position adjacent to the metal atom at a distance, for instance, of two—three bond lengths.

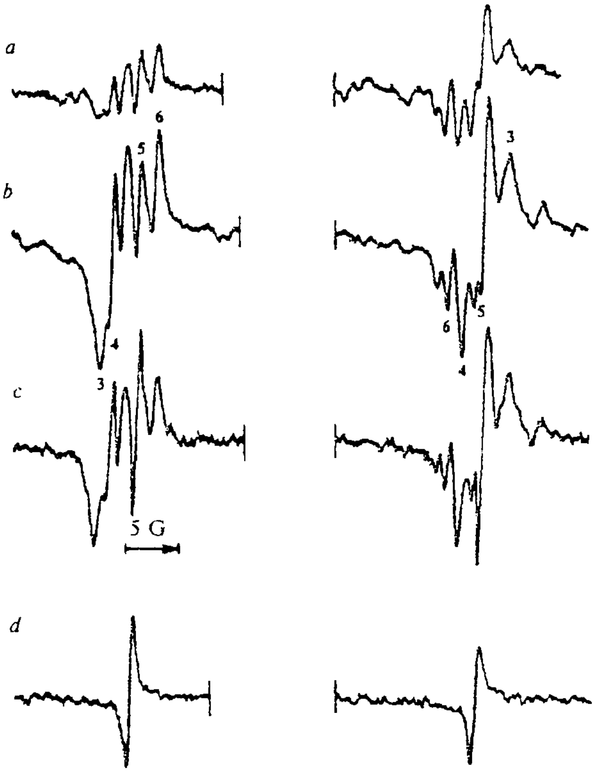
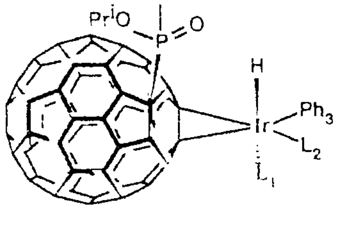


Fig. 1. ESR spectra of isomers $(Pr^iO)_2(O)P$—$(C_{60})IrH(CO)(PPh_3)_2$ (**3**—**6**) recorded with an interval of 8 min in the UV-irradiation of the reaction mixture (300 K) (*a*—*c*) and of $(Pr^iO)_2(O)P$—$(C_{60})^{\bullet}$ formed 5 min after heating at 370 K (*d*).



This assumption is supported by the increase in the constant of HFI with the nucleus of the phosphorus atom of the phosphoryl radical as compared with the analogous constant for $C_{60}P(O)(OPr^i)_2$,[5] since one of the double bonds nearest to the radical center is excluded from conjugation because of the addition of the metallocomplex (*cf.* Ref. 2). It is known that the density of the unpaired electron in the fullerenyl radicals is mainly delocalized over two six-membered cycles adjacent to the C—CR bond.[6,7] Demetalation of the metallocomplex occurs when the sample is heated to 370 K and the ESR spectrum of $^{\cdot}C_{60}P(O)(OPr^i)_2$ radical is recorded (Fig. 1, *d*).

An analogous picture is observed for the radical adducts of the phosphoryl radicals with metallocomplex 2. A broad signal (a_P = 62.7 G, g = 2.0028) dominates immediately after photolysis was begun.

Thus, it is likely that a characteristic feature of the radical adducts of metallocomplexes of C_{60} with Ir is the addition of the phosphoryl radicals at a distance of two—three bond lengths from the metal atom. This might be caused by a stronger distortion of the polyhedron in the iridium metallocomplex than that in the complexes of fullerene with Pt and Pd because of stronger binding of Ir with fullerene.

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Reaction of hydroxyiminoacetophenone with *p*-toluenesulfonyl chloride and an X-ray diffraction study of the reaction product

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2-Benzoyloxy-2-phenylmalononitrile is formed instead of the expected oxime tosylate in the reaction of hydroxyiminoacetophenone with *p*-toluenesulfonyl chloride. The structure of the product was confirmed unambiguously by X-ray diffraction analysis.

Key words: hydroxyiminoacetophenone; *p*-toluenesulfonyl chloride; 2-benzoyloxy-2-phenylmalononitrile; X-ray diffraction analysis.

Previously,[1] the *p*-toluenesulfonate of oxomalononitrile oxime used for the synthesis of substituted cyanopyrazines[2] has been prepared by tosylation of hydroxyiminomalononitrile. We attempted to synthesize the *p*-toluenesulfonate of phenylglyoxal oxime in order to use it for similar purposes. However, the ^{1}H NMR

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