Stable radical adducts of diisopropylphosphoryl radicals with fullerene complexes $(\eta^2 - C_{60})Os(CO)(PPh_3)_2(CNBu^t)$ and $(\eta^2 - C_{70})Os(CO)(PPh_3)_2(CNBu^t)$

B. L. Tumanskii, R. G. Gasanov, M. V. Tsikalova, A. V. Usatov, E. V. Martynova, and Yu. N. Novikov*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation. Fax: +7 (095)135 5085. E-mail: novik@ineos.ac.ru

It was determined by ESR spectroscopy that the UV irradiation of toluene solutions containing $Hg[P(O)(OPr^i)_2$ and the complex $(\eta^2-C_{60})Os(CO)(PPh_3)_2(CNBu^t)$ produces six stable regioisomeric adducts of phosphoryl radicals with complexes, which are not demetallated under UV irradiation and do not dimerize in the absence of UV irradiation. This is caused by the addition of the phosphoryl radicals to the carbon atoms of fullerene localized near the metal-containing moiety. The addition of the phosphoryl radicals to $(\eta^2-C_{70})Os(CO)(PPh_3)_2(CNBu^t)$ gives rise to the formation of nine stable regioisomeric radical adducts. A comparison of the composition of regioisomers of the radical adducts of C_{70} with the phosphoryl radicals, which were formed directly from C_{70} and from the radical adducts of $\eta^2-C_{70}Os(CO)(PPh_3)_2(CNBu^t)$ by the demetallation of the latter, revealed an orienting effect of the osmium-containing moiety on the addition of the phosphoryl radicals to the fullerene complex.

Key words: fullerene, radical reactions, metal complex, ESR, phosphoryl, stable radicals, regioisomers.

A characteristic feature of fullerenes is the ability to add readily free radicals due to many weakly conjugated double bonds. This property is useful for both preparative chemistry and studying the mechanism of radical processes involving fullerenes in the chemistry of polymers^{1,2} and in biological processes.³

The addition of a radical to a C_{60} molecule affords a radical adduct of the same type, because all carbon atoms in C₆₀ are equivalent. Organic or metal complex fullerene derivatives exhibit a distortion of the fullerene cage, the appearance of groups of nonequivalent carbon atoms, and, as a consequence, the formation of a set of regioisomeric adducts of a radical with these derivatives. The addition to these molecules of radicals with a high hyperfine coupling (HFC) constant (for instance, phosphorus-centered radicals) makes it possible to use them as labels ("paramagnetic reporters") and to obtain an information on the regiochemistry of radical addition from the observed HFC constant value.^{4,5} The radical phosphorylation of platinum and palladium complexes with fullerene $(\eta^2 - C_{60})M(PPh_3)_2$ (M = Pt (1a), Pd (1b)) results in their fast demetallation, which does not allow one to study regioselectivity of radical addition to these compounds.^{4,6} The radical adducts $(\eta^2-C_{60})IrH(CO)(PPh_3)_2$ (1c) were found to be more stable. In this case, the phosphoryl radicals add predominantly to the fullerene half-sphere bearing the metal-containing moiety.⁷ However, the addition regioselectivity was not revealed in detail, because the spin-adducts that formed dimerize when irradiation is ceased.

We continued a search for stable spin-adducts for studying in more detail the regioselectivity of addition of phosphoryl radicals to fullerene complexes. In this work, we studied the addition of diisopropylphosphoryl radicals to complexes $(\eta^2-C_{60})Os(CO)(PPh_3)_2(CNBu^t)$ (2) and $(\eta^2-C_{70})Os(CO)(PPh_3)_2(CNBu^t)$ (3) and studied specific features of ESR spectra of the spin-adducts formed.

Experimental

ESR spectra were recorded on a Varian-E12a radiospectrometer. Toluene solutions of reaction mixtures in quartz ampules were thoroughly evacuated. Samples were irradiated with the focused light from a DRSh-1000 high-pressure mercury lamp in the cavity of an ESR spectrometer.

Osmium complexes 2 and 3 were synthesized according to previously described procedures.⁸

Synthesis of bis(diisopropylphosphoryl)mercury, Hg[P(O)(OPrⁱ)₂]₂ (4). Anhydrous benzene (120 mL), HgO (4 g, 0.018 mol), and (PriO)₂P(O)H (6 g, 0.036 mol) were placed in a two-neck flask equipped with a condenser and a thermometer. The mixture was refluxed with distilling off the solvent and water formed. After 100 mL of the solvent were distilled off, the resulting mixture was left for 16 h. A light yellow solid product was extracted with hot hexane (5×30 mL), and the resulting

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solution was decanted from the precipitate and evaporated on a rotary evaporator to 1/3 of the primary volume. The precipitate formed was filtered off and dried. Complex **4** was obtained in 59% yield (5.7 g).

Results and Discussion

(C₆₀-Fullerene-1,2-diyl)carbonyl-*tert*-butylisonitrilebis(triphenylphosphine)osmium, $(\eta^2-C_{60})Os(CO)(PPh_3)_2$ -(CNBu^t) (2). Irradiation of a solution of complex 2 and compound 4 in toluene (1 : 1.5 mol/mol) in the cavity of an ESR spectrometer produced six regioisomeric spinadducts (Scheme 1, 5a-f), four of which (5a-d) being predominant (Fig. 1). The spin-adducts are characterized by the following magnetic resonance parameters:

Compound	$a_{\rm P}/{\rm G}$	g
5a	61.0	2.0078
5b	58.5	2.0078
5c	53.0	2.0075
5d	50.0	2.0079

The absence of distinct splitting from two minor regioisomers **5e**,**f** did not allow us to determine their magnetic resonance parameters.

Scheme 1

$$Hg[P(O)(OPr^{i})_{2}]_{2} \xrightarrow{hv} 2 P(O)(OPr^{i})_{2} + Hg$$

 $\begin{array}{l} \textbf{2} + `P(O)(OPr^{i})_{2} \rightarrow \\ \rightarrow [(\eta^{2} - `C_{60})Os(CO)(PPh_{3})_{2}(CNBu^{t})][P(O)(OPr^{i})_{2}] \\ \textbf{5a-f} \end{array}$

The spin-adducts of the phosphoryl radicals with complex 2 differ substantially in properties and characteristics from all known metal complexes spin-adducts. First, after irradiation is ceased, the intensity of signals from regioisomers 5a-f remains unchanged, *i.e.*, the spin-adducts are stable. In addition, the ESR spectra of regioisomers **5a-d** exhibit a noticeable positive shift of the g factor (2.0075–2.0079) relatively to those of $C_{60}P(O)(OPr^{i})_{2}$ (g = 2.0023) and spin-adducts **1a,b** (g = 2.0017 - 2.0032)due to the coupling of an unpaired electron with the osmium atom having a higher spin-orbital moment. Finally, the HFC constants of an unpaired electron with the phosphorus nucleus for isomers 5c-d (50-53 G) are lower than similar constants for $C_{60}P(O)(OPr^{i})_{2}$ ($a_{P} =$ 63.5 G) and spin-adducts 1c ($a_{\rm P} = 58.5 - 68$ G). These data indicate that the phosphoryl radical adds to the same fullerene half-sphere containing the metal moiety, because the above difference in the magnetic resonance parameters of the spin-adducts can be observed only in this case. In addition, the parameters of spin-adducts 2 indicate a higher delocalization of an unpaired electron in 5a-d compared to the C₆₀ spin-adducts and the spin-



Fig. 1. ESR spectrum of the radical adducts of $(\eta^2-C_{60})Os(CO)(PPh_3)_2(CNBu^t)$ with the phosphoryl radicals. Minor and nonidentified isomers are marked by asterisks.

adducts of C_{60} with the platinum and palladium complexes.

Two main factors can be distinguished among those determining the addition of the phosphoryl ligand to the fullerene half-sphere containing the metal moiety: (1) electronic factor related to a partial transfer of the electron density from the metal atom to the fullerene molecule in complex 2 and (2) distortion of the carbon polyhedron near the site of metal-containing moiety addition. Calculations show* that the negative charge is localized in the half-sphere containing the metal-containing moiety, and the attack of the phosphoryl radical is directed to the same half-sphere. In fact, according to the data of UV spectroscopy,⁸ complex 2 exhibits the highest electron density transfer from the metal atom to fullerene compared to the Pt, Pd, and Ir complexes, whose spinadduct formation has been studied earlier.^{6,7} The carbon polyhedron is distorted due to complex formation primarily near the site of metal-containing moiety addition.⁹ These factors lead to the appearance of more planar regions directly in the vicinity of the metal-containing moiety, favoring the delocalization of an unpaired electron, its interaction with the osmium atom, and, as a consequence, spin-adduct stabilization.

Since the regioisomers of the radical adducts have almost the same g factor, we can assume that the spin density is localized at close range of the metal (Fig. 2).

^{*} R. G. Gasanov, B. L. Tumanskii, V. I. Sokolov, I. V. Stankevich, A. L. Chistyakov, and L. I. Go, a material is to be published.



Fig. 2. Structure of the $C_{60}Os(CO)(PPh_3)_2(CNBu^1)$ complex. Possible sites of phosphoryl radical addition are indicated by arrows.

For all regioisomers observed, the main condition for close values of considerable shifts of the g factor compared to that for **1c** is the same spin density on the osmium atom in these isomers.

The distortion of the fullerene cage is not the main reason for the addition of the phosphoryl radicals near the metal complex, because a similar deformation is also observed for organic fullerene derivatives, whose radical phosphorylation includes no preferential attack to a site next to the added organic moiety. Therefore, the electronic factors exert the main effect on the regiochemistry of addition of phosphoryl radicals.

The absence of demetallation of complex 2 upon its interaction with the phosphoryl radical is related, most likely, to the fact that the osmium atom in this complex has an octahedral ligand environment and is coordinately saturated. This prevents a direct attack of the phosphoryl radical at the metal atom, which, in the opinion of the authors,⁶ is the main reason for the demetallation of complexes 1a,b.

The resistance of the spin-adducts of complex 2 to dimerization can be caused by both a substantial delocalization of an unpaired electron and steric hindrance created by the ligands at the osmium atoms and the isopropioxy groups of the phosphoryl radical. An increase in the unpaired electron delocalization in the spin-adducts of complex 2 enhances their resistance to dimerization, as shown¹ for some isomers of the radical adducts of C_{70} and C_{76} .

(C₇₀-Fullerene-1,2-diyl)-*tert*-butylisonitrile-bis(triphenylphosphine)osmium, $(\eta^2-C_{70})Os(CO)(PPh_3)_2$ -(CNBu^t) (3). It is known¹⁰ that a C₇₀ molecule contains five types of nonequivalent atoms: A, B, C, D, and E (Fig. 3). Diisopropylphosphoryl radicals add to three of



Fig. 3. Fullerene C_{70} (A–E are nonequivalent carbon atoms).

them (**B**, **C**, and **D**) to form spin-adducts with the following parameters:

1		
Atom	$a_{\rm P}/{\rm G}$	g
B	70.5	2.0031
С	66.5	2.0027
D	55.25	2.0028

The ratio of these regioisomers is $\sim 1 : 1 : 1.5$. After irradiation was ceased, the radical adduct of phosphoryl radical addition to vertex **D** remains stable due to a higher unpaired electron delocalization, and other two isomers recombine. It could be expected that the ratio of regioisomers of phosphoryl radical addition to vetices **B**, **C**, and **D** in the C₇₀ complexes would be different due to the orienting effect of the metal-containing moiety. Therefore, we studied the addition of the phosphoryl radical to complex **3** and the composition of regioisomers of the phosphoryl spin-adducts of C₇₀ formed upon the demetallation of the radical adduct of complex **3**.

After the irradiation in the spectrometer cavity of a toluene solution of a mixture of complexes 3 and 4 (1:1.5 mol/mol), nine predominant regioisomers of the fullerenyl radicals were found (Scheme 2, 6a-i) (Fig. 4). They are characterized by the following magnetic resonance parameters:

Radical	$a_{\rm P}/{\rm G}$	g	Radical	$a_{\rm P}/{\rm G}$	g
6a	81.8	2.0079	6f	55.5	2.0037
6b	82.5	2.0058	6g	52.5	2.0037
6c	71.0	2.0073	6h	49.4	2.0037
6d	69.5	2.0044	6i	41.25	2.0035
6e	45.5	2.0074			

Scheme 2

$\begin{array}{l} \textbf{3} + `P(O)(OPr^{i})_{2} \rightarrow \\ \rightarrow (\eta^{2} \cdot `C_{70})Os(CO)(PPh_{3})_{2}(CNBu^{t})[P(O)(OPr^{i})_{2}] \\ \textbf{6a-i} \end{array}$

All isomers observed are stable, and signals from the regioisomers remain unchanged after the irradiation is ceased, *i.e.*, as in the case of complex 2, the phosphoryl radicals add to complex 3 near the metal-containing moi-



Fig. 4. ESR spectrum of the spin-adduct of $(\eta^2 - C_{70})Os(CO)(PPh_3)_2(CNBu^t)$ with the phosphoryl radical.

ety. The addition of trifluoroacetic acid to a solution containing spin-adduct **6a**—**i** induces their demetallation, and the ESR spectra exhibit only one signal corresponding to the spin-adduct of C_{70} formed due to phosphoryl radical addition to vertex **D**. However, when this solution is irradiated with the light ($\lambda > 620$ nm) inducing the dissociation of dimers of the fullerenyl radicals but producing no



Fig. 5. ESR spectra of the adducts of C_{70} with the phosphoryl radicals obtained by the demetallation of the radicals adducts of $(\eta^2-C_{70}Os)(CO)(PPh_3)_2(CNBu^t)$ phosphorylation (*a*) and direct phosphorylation of C_{70} (*b*).

phosphoryl radicals from **3**, the ESR spectrum exhibits three regioisomeric spin-adducts of C_{70} in the ratio **B** : **C** : **D** = 1 : 5 : 2.6 (Fig. 5, *a*). A comparison of this ratio with a similar ratio for the spin-adducts formed by the addition of the phosphoryl radical to unsubstituted fullerene C_{70} (1 : 1 : 1.5) (Fig. 5, *b*) demonstrates the orienting effect of the metal-containing moiety on the direction of phosphoryl radical addition to complex **3**.

Thus, the study of the radical reactions involving the osmium complexes of fullerenes C_{60} and C_{70} allowed us to obtain the first stable spin-adducts of phosphoryl radicals with metal complex fullerene derivatives, characterize them, and study the orienting role of the metal-containing moiety in the addition of free radicals to the fullerene cage.

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