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Regioselectivity of the addition of $^{\cdot}CCl_3$ and $^{\cdot}Bu^t$ radicals to $(\eta^2\text{-}C_{70})[Os(CO)(PPh_3)_2(CNBu^t)]_n$ (n = 1, 2): an ESR study

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The addition of $^{\cdot}CCl_3$ and $^{\cdot}Bu^t$ radicals to $(\eta^2\text{-}C_{70})Os(CO)(PPh_3)_2(CNBu^t)$ (**1**) and $(\eta^2\text{-}C_{70})[Os(CO)(PPh_3)_2(CNBu^t)]_2$ (**3**) was studied by ESR spectroscopy. The metal fragment in complex **1** does not influence the regioselectivity of the addition of the radicals to it. The stability of the spin adducts formed upon addition of free radicals to complexes **1** and **3** is mainly governed by delocalization of the unpaired electron over three hexagonal rings.

Key words: metallofullerenes; ESR spectroscopy; electronic effects; phosphoryl, trichloromethyl, and *tert*-butyl radicals; regioselectivity; stability.

A promising application of metal-complex derivatives of fullerenes is to use them in organic photovoltaic devices (OPD).[1,2] This involves the study of their reactivities toward various types of free radicals. The importance of such investigations is determined by the possibility of generating free radicals of OPD on exposure to sun light.[3]

The factors influencing the reactivity, regioselectivity of the addition of free radicals to the C_{60} fullerene derivatives, and stability of the spin adducts (SAs) that are formed were established earlier.[4] They include: 1) pyramidality of carbon atoms of particular bonds (it is due to deformation of the fullerene cage upon the addition of a radical and influences the direction of addition of radicals); 2) steric properties of the ligands and groups bound to the atom attached to fullerene, because substituents can shield the carbon atoms of the *cis-n* bonds (n = 1, 2, 3) (Fig. 1) and thus prevent free radical from being added to them; 3) the donor-acceptor properties of the metal fragment or ogranic group attached to fullerene, because they can influence the direction of addition of radicals and the stability of the SA; and 4) the steric and polar properties of the radicals that add to fullerenes.

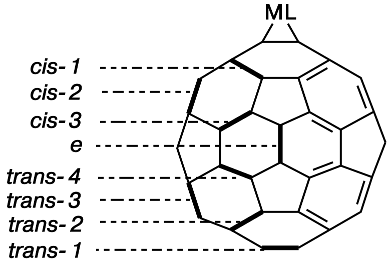

Fig. 1. Reactive centers in the C_{60} fullerene derivatives (M is a metal, L is a ligand).

In contrast to the symmetric fullerene C_{60} where all carbon atoms are equivalent, in the fullerene C_{70}, there are five nonequivalent carbon atoms A, B, C, D, and E (Fig. 2). Therefore, the regioselectivity of addition of free radicals to the C_{70} fullerene derivatives also depends on the stability of particular SA, which is determined by delocalization of the unpaired electron. For example, a SA was detected by ESR spectroscopy upon photochemical addition of phosphoryl radicals to C_{60}. The signal of this SA disappeared a few seconds after irradiation was switched off. When phosphoryl radicals reacted with C_{70}, the ESR spectra exhibited signals of three regioisomers **A**, **C**, and **D** formed by the addition of the radicals to the atoms A, C, and D, respectively. The regioisomer **D** was stable, be-

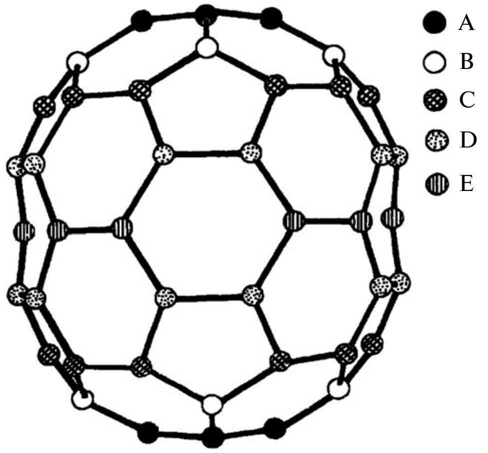

Fig. 2. Reactive centers of the C_{70} fullerene.

[†] Deceased.

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cause its signals were observed for a rather long time after switching off the irradiation, while the signals for isomers **A** and **C** disappeared after a few seconds. The stability of the isomer **D**, in contrast to the isomers **A** and **C**, was explained by delocalization of the unpaired electron over three hexagonal rings.[5] Therefore, investigations of the individual effects of all factors mentioned above on the reactivity and regioselectivity of addition of free radicals to the C_{70} derivatives are undoubtedly of interest.

It follows from the X-ray diffraction data for the complex $(\eta^2\text{-}C_{70})Os(CO)(PPh_3)_2(CNBu^t)$ (**1**)[6] (see Experimental) that the atoms C(58), C(65), C(67), and C(68) (Fig. 3) in the lower hemishpere (344.1—347.1°) and the atom C(15) (346.2°) in the upper hemishere of **1** are characterized by the highest pyramidality. In contrast to complex **1**, for $(\eta^2\text{-}C_{60})Os(CO)(PPh_3)_2(CNBu^t)$ (**2**) the highest pyramidality was obtained for some atoms of the *cis*-**1** and *cis*-**2** bonds.[7] According to quantum chemical calculations of the Mulliken effective atomic charges on carbons in complexes **1** and **2**, the positive charge is localized on the osmium atom (+1.67 and +1.70 a.u, respectively). The charges on the carbon atoms bound to the metal atom are negative (–0.518; –0.539 a.u. and –0.501; –0.538 a.u., respectively). These two complexes have significantly different charge distributions for other carbon atoms of the fullerene hemisphere bound to the metal fragment. Namely, in complex **1**, the maximum negative charges are on the carbon atoms E (−0.097 (C(21)), −0.080 (C(36)) and −0.077 a.u. (C(20)), B (C(4)), and C (−0.050 a.u. (C(17)) (see Fig. 2; the charges on other carbon atoms of the C_{70} cage are positive or have negative values in the range from −0.0205 to −0.0001 a.u.). In complex **2**, the negative charges are located on the carbon atoms of the *cis*-**1** (−0.049—−0.032 a.u.) and *cis*-**2** (−0.033 a.u.) bonds.[7] It follows that in the case of complex **2**, both the pyramidality and donor-acceptor properties of the metal fragment will favor the addition of free radicals to the carbon atoms of the *cis*-**1** and *cis*-**2** bonds. In the case of complex **1**, only the donor-acceptor properties of the metal fragment will influence the regioselectivity of the addition of radicals to the hemisphere bound to the metal fragment. In order to confirm these assumptions, we studied the addition of the $^{\cdot}CCl_3$ (R^1) and $^{\cdot}Bu^t$ (R^2) radicals to complexes **1** and $(\eta^2\text{-}C_{70})[Os(CO)(Pph_3)_2(CNBu^t)]_2$ (**3**). The choice of these radicals is due to the fact that they are sterically similar but differ appreciably in electrophilicity.

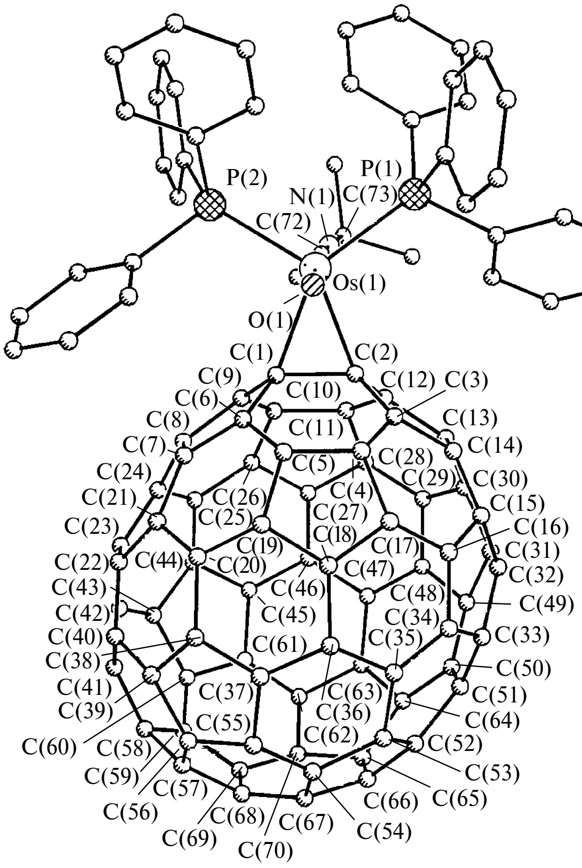

Fig. 3. The structure of complex **1**.

The aim of the present work is to study the effect of the metal fragment on the regioselectivity of addition of the radicals R^1 and R^2 to complexes **1** and **3**, as well as to interpret the results obtained earlier.[8,9]

Experimental

The ESR spectra of the spin-adducts of the radicals R^1 and R^2 with complexes **1** and **3** were recorded on a Varian E-12A spectrometer. Cylindrical glass tubes containing solutions of complexes **1** or **3** in benzene and toluene were degassed in the presence of $BrCMe_3$ or CCl_4 and $Re_2(CO)_{10}$ using the "freeze—pump—thaw" technique (several cycles). The tubes were irradiated with a DRSh-1000 lamp in the spectrometer cavity at ~20 °C. The 366 nm frequency band was cut using a glass light filter. The *g*-factors of the radicals under study were calculated using a Varian pitch ($g = 2.0028$) as a reference.

The radicals R^2 or R^1 were generated by abstraction of Br or Cl atoms from $BrCMe_3$ ($[BrCMe_3]_0 = 0.1\text{—}0.3$ mol L^{-1}) or CCl_4 ($[CCl_4]_0$ = 0.2—0.4 mol L^{-1}) molecules, respectively, by $^{\cdot}Re(CO)_5$ radicals formed in the photochemical decomposition of $Re_2(CO_{10})$ ($[Re_2(CO)_{10}]_0 = (0.5\text{—}1) \cdot 10^{-3}$ mol L^{-1}).[10] The starting concentrations of metallofullerenes in solutions of the samples under study were 10^{-3} mol L^{-1}.

Spectra were simulated by means of the Simfonia program.

Complexes **1** and **3** were synthesized according to a known procedure.[6] Complexes **1** and **3** were characterized by elemental analysis. Their structures were confirmed by UV, IR, and NMR (^1H, ^{31}P) spectroscopies. The structure of complex **1** was confirmed by X-ray diffraction analysis.

Quantum chemical calculations of complex **1** were performed by the density functional theory in the pseudopotential approximation with the PBE exchange-correlation functional

(DFT-PBE)[11] using the PRIRODA program[12] based on the X-ray diffraction data.

Results and Discussion

Based on the NMR data, one can conclude that complex **1** forms through addition of the metal fragment to the A—B bond of the C_{70} molecule and to the C—C bond (minor product)[6] (see Fig. 3). It follows from Fig. 3 that there will be three isomers due to the addition of the metal fragment to the carbon atoms of the C(1)—C(2), C(5)—C(6), and C(9)—C(10) bonds. The addition of a radical to the carbon atom, for example, the C(14) atom will lead to different effect of the metal fragment on the radical center at the C(3) atom in particular isomers. It follows from Figs 2 and 3 that the carbon atoms C, D, and E are nonequivalent (see Ref. 5). Therefore, the effect of the metal fragment on the radical centers in the SA formed by adding a free radical to these atoms will be different.

The ESR spectrum of a solution of the SA $\mathbf{1}\cdot R^1$ displays a superpositon of the signals for twelve isomers, as was determined by comparing the experimental and simulated spectra (Fig. 4, Table 1). A large number of signals with close values of the *g*-factors precludes unambiguous assignment of individual signals to particular regioisomers. Nevertheless, these regioisomers can be classified tentatively in several groups based on the *g*-factor values. Three signals with the *g*-factors in the region (2.0032±0.0004) (see Table 1) in the ESR spectrum are close to the values of three *g*-factors of the spin adducts of the radicals R^1 with C_{70} (see Ref. 13). Consequently, they represent a superposition of the signals for the regioisomers where the radical center is far from the metal fragment. Such regioisomers can be formed by adding radicals R^1 to carbon atoms of fullerene hemisphere in complex **1** containing no metal fragment. The remaining signals with $g > 2.0041$ can be attributed to the SAs formed upon addition of the radicals R^1 to the carbon atoms bearing maximum negative charge in the upper hemisphere, *viz.*, the atoms B, C, and E positioned close to the metal fragment. Probably, the signals with $g = 2.0041—2.0054$ characterize the SAs formed upon addition of the radicals to the carbon atoms E; as a result, the radical center is on the carbon atoms D. These SAs are analogous to those formed by adding the radicals R^1 to the carbon atoms of the *cis*-**2** and *cis*-**3** bonds of complex **2** (see Table 1). The spin adducts with $g = 2.0060—2.0073$ are formed in the addition of the radical R^1 to the carbon atoms B and C, *i.e.*, the radical center will be near to the atoms A and B. These SAs are close, according to their parameters, to the SAs formed upon addition of the radicals R^1 to the carbon atoms of the *cis*-**1** and *cis*-**2** bonds in complex **2** (see Table 1).

All spin adducts of the radicals R^1 with complex **1** are quite stable and their signals can be observed over several weeks. Particular regioisomers have different stabilities due to delocalization of the unpaired electron over two or three hexagonal rings. This also allows one to assign particular signals to one or another regioisomer. Upon re-recording the ESR spectrum of a solution obtained upon addition of radical R^1 to complex **1** and storage in the dark for 7 days, the intensities of the SA signals decreased significantly, except for the signals with the *g*-factors in the region of

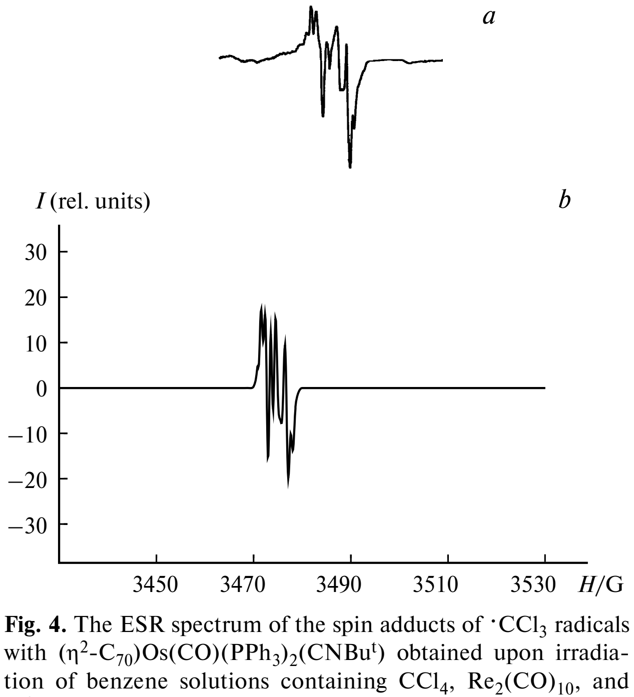

Fig. 4. The ESR spectrum of the spin adducts of $^{\cdot}CCl_3$ radicals with $(\eta^2\text{-}C_{70})Os(CO)(PPh_3)_2(CNBu^t)$ obtained upon irradiation of benzene solutions containing CCl_4, $Re_2(CO)_{10}$, and $(\eta^2\text{-}C_{70})Os(CO)(PPh_3)_2(CNBu^t)$ at 366 nm (*a*) and the simulated spectrum (*b*).

Table 1. The *g*-factor values of the regioisomers of the SAs of radicals R^1 and R^2 with the metallofullerenes **1**—**3**

Regioisomer	*g*-Factor
$\mathbf{2}\cdot R^1$	*cis*-1: 2.0114, 2.0107, 2.0101, 2.0087; *cis*-2: 2.0080, 2.0071, 2.0061, 2.0053; *cis*-3,e: 2.0043; *trans*-*n*: 2.0037
$\mathbf{1}\cdot R^1$	2.0073, 2.0071, 2.0070, 2.0065, 2.0063, 2.0060, 2.0054, 2.0049, 2.0047, 2.0044, 2.0041, 2.0036
$\mathbf{2}\cdot R^2$	*cis*-1: 2.0091, 2.0085, 2.0073; *cis*-2: 2.0068, 2.0062, 2.0050; *cis*-3,e: 2.0034; *trans*-*n*: 2.0028*
$\mathbf{1}\cdot R^2$	2.0027,** 2.0023,** 2.0020**
$\mathbf{3}\cdot R^2$	2.0027,** 2.0023,** 2.0020,** 2.0037, 2.0039, 2.0041, 2.0048

* $a_H = 0.17$ G, A (see Ref. 4). ** $a_H = 0.15$ G.

2.0054—2.0036. These results agree with the assignment of these signals to the regioisomers formed by adding radicals R^1 to the atoms E of complex **1** (see above).

In the reaction of radicals R^1 with complex **3**, the ESR spectrum displays the same signals as in the case of complex **1**, the only difference being the lack of clear splitting from particular SAs. It should be noted that the intensitites of the signals in the region $g = 2.0054$—2.0040 increase appreciably with an increase in the irradiation time. One can assume that these signals should be assigned the regioisomers, in which the unpaired electron is delocalized over three hexagonal rings. In other words, these regioisomers are formed by adding radicals R^1 to the carbon atoms D and E of complex **3**.

The addition of radicals R^2 to complex **1** gives rise to the ESR spectrum displaying the signals for three regioisomers characterized by the following magnetic resonance parameters: $a_H = 0.15$ G, $g^1 = 2.0020$, $g^2 = 2.0023$, and $g^3 = 2.0027$ (see Table 1). These parameters are close to the corresponding parameters of the SAs of the radicals R^2 with C_{70} (see Ref. 13).

Signals for nine regioisomers were observed upon addition of the radicals R^2 to complex **2**.[7-9] The hyperfine splitting due to the interaction of the unpaired electron with protons was observed for only one of them. All remaining regioisomers are characterized by singlets in the ESR spectrum. It is believed that the absence of splitting on protons is a result of delocalization of the unpaired electron caused by its spin-orbital interaction with the osmium nucleus. Thus, these are the SAs formed by addition of radicals to the *cis-n* bonds ($n = 1, 2$) of complex **2**. It follows from the comparison of these results with those obtained in the present work that the metal fragment in complex **1** has no effect on the regioselectivity of addition of the radicals R^2. Such a difference in the ESR spectra of the SAs of the radicals with complexes **2** and **1** can be explained as follows. As mentioned above, the C(58), C(65), C(67), and C(68) atoms in the lower hemisphere and the C(15) atom in the upper hemishpere are characterized by the highest pyramidality among the carbon atoms in complex **1**. Therefore, the radicals R^2 will be added to these atoms. Even upon addition to the C(15) atom of the complex, the radical center will be far from the metal fragment. Therefore, the radicals R^2 add to those carbon atoms of complex **1** that are far from the metal fragment.

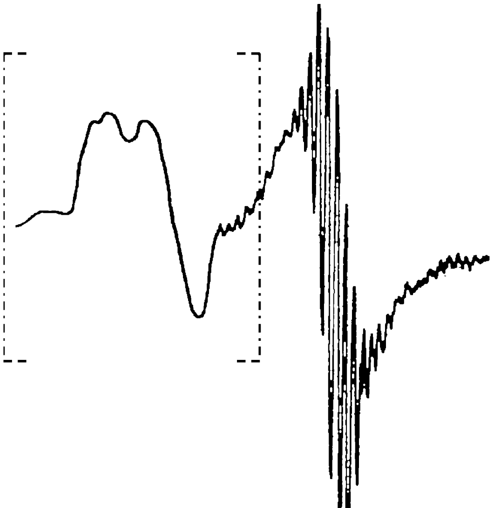

Fig. 5. The ESR spectrum of the spin adducts of $^{\cdot}Bu^t$ radicals with complex **3** obtained upon irradiation of benzene solutions containing $BrBu^t$, $Re_2(CO)_{10}$, and $(\eta^2\text{-}C_{70})[Os(CO)(PPh_3)_2(CNBu^t)]_2$ at 366 nm. The signals that are absent in the ESR spectrum upon the addition of $^{\cdot}Bu^t$ to complex **1** are represented by the dashed line.

The ESR spectrum of the solution recoveded upon addition of radicals R^2 to complex **3** also exhibits singlets with *g*-factors of 2.0037, 2.0039, 2.0041, and 2.0048 along with the signals observed in the reaction of radicals R^2 with **1** (see Fig. 5).

The structure of complex **3** is unavailable. However, one can assume that the second metal fragment favors a decrease in the electron density on the hydrogen atoms of the Bu^t group in some SAs of the radicals R^2 with **3**, which causes a decrease in the a_H value. As a consequence, no hyperfine splitting on protons is observed.

Based on the assignment of signals to particular regioisomers of the complex $(\eta^2\text{-}C_{60})Os(CO)(PPh_3)_2(CNBu^t)$ (**2**),[7] one can assume that the signals with the *g*-factors of 2.0041 and 2.0048 arise from the addition of radicals R^2 to the carbon atoms of the bonds near the metal fragments (see Table 1).

The results obtained allows one to assign the signals to the particular regioisomers formed in the addition of the phosphoryl radical $(O)^{\cdot}P(OPr^i)_2$ (R^3) to complex **1** that have been described earlier.[8] The addition of R^3 to complexes **1** and **2** gives rise to ESR spectra with nine and six doublets, respectively. They were characterized by the *g*-factors in the regions 2.0079—2.0035 and 2.0075—2.0070, respectively. All regioisomers formed in these reactions were stable. As noted above, for these two complexes, the Mulliken effective charge distributions over the carbon atoms bound to the metal atom differ only slightly. To explain the large difference in the values of the *g*-factors of regioisomers on going from complex **2** to complex **1**, one can assume that four radicals characterized by the *g*-factors in the region 2.0035—2.0037 (this is close to the *g*-factors of the SAs of phosphoryl radicals with C_{70} (see Ref. 5)) are produced by adding radicals R^3 to the carbon atoms E of complex **1** (see Fig. 6, *a*). In this case, the radical center is far from the metal fragment. Two regioisomers with $g = 2.0044$ and $g = 2.0058$ are produced by the addition of radicals R^3 to the atoms D in **1** (see Fig. 6, *b*). In these cases, the effect of the metal fragment on the

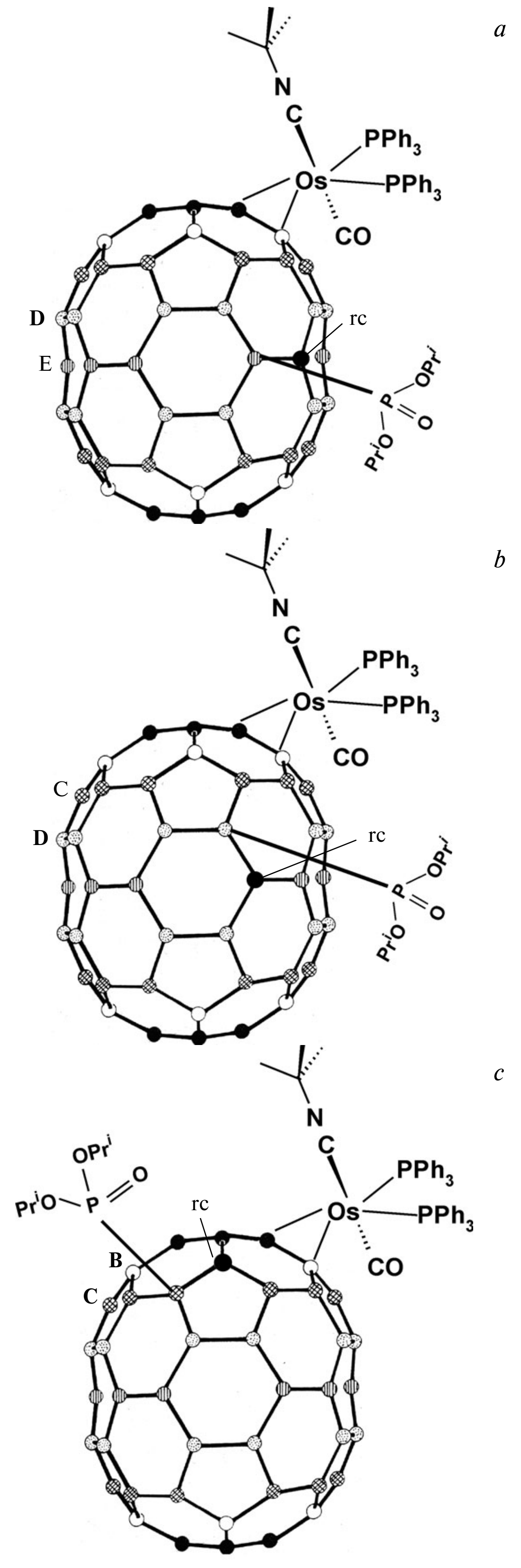

Fig. 6. The spin adducts of the phosporyl radicals with complex **1** (rc is the radical center).

values of the g-factors will be insignificant. However, due to delocalization of the unpaired electron over three hexagonal rings, all these six regioisomers will be stable. The signals with the g-factors 2.0079, 2.0074, and 2.0073, which are very close to the g-factors of the SAs of the radicals R^3 with complex **2**, belong to the SAs formed by the addition of radicals R^3 to the carbon atoms positioned near the metal fragment. These can be the atoms B and C of complex **1** (see Fig. 6, *c*). In this case, the metal fragment and the phosphoryl radical will shield the radical center in a such way that dimerization of SAs is hindered considerably, as is observed for complex **2**.

Based on the results obtained, one can draw the following conclusions.

The addition of electrophilic radical $^{\cdot}CCl_3$ to complexes **1** and **3** is mainly governed by the electron-donating properties of the osmium fragment. Stabilization of the SAs occurs through both delocalization of the electron density of the unpaired electron over the metal fragment and delocalization of an electron over three hexagons.

The osmium fragment has little effect on the direction of addition of the nucleophilic radical Bu^t to complex **1**. This direction is determined by the possibility of formation of the SAs where the unpaired electron is delocalized over three six-membered rings. This delocalization determines the stabilities of the SAs that are formed.

The addition of Bu^t to complex **3** having two metal fragments results in the formation of four additional SAs. In these SAs, the radical centers are near the osmium fragments: which are involved in delocalization of the unpaired electron.

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