Russian Chemical Bulletin, International Edition, Vol. 56, No. 7, pp. 1351—1358, July, 2007 1351

Influence of the nature of ligands in iridium complexes with C_{60} fullerene and $^{\bullet}P(O)(OPr^{i})_2$, $^{\bullet}CMe_3$, and $^{\bullet}CCl_3$ radicals on regioselectivity of addition and stability of spin-adducts formed: an EPR study

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The addition of $^{\bullet}P(O)(OPr^{i})_2$ (R^1), $^{\bullet}CMe_3$ (R^2), and $^{\bullet}CCl_3$ (R^3) radicals to metallofullerenes (η^2-C_{60})IrH(CO)(CNBu^t)$_2$(*o*-$HCB_{10}H_9CCH_2PPh_2$-B,P) (**1**), (η^2-C_{60})IrH(CO)(DIOP) (DIOP is (4*R*,5*R*)-(+)-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane, **2**), and (η^2-C_{60})IrH(CO)(PPh_3)$_2$ (**3**) was studied by EPR spectroscopy. A stability study of spin adducts (SAs) of R^1 radicals with complexes **1** and **2** showed that when the reactions are initiated by illumination with 366-nm light, the EPR spectra exhibit only signals of those isomers that are formed upon attack of the R^1 radicals on the carbon atoms of the *cis-1* and *cis-2* bonds (*i.e.*, carbon atoms of the fullerene hemisphere to which the metallofragment is attached). Investigations of the reactions of R^2 and R^3 radicals with complexes **1**—**3** initiated with 366-nm light made it possible to detect (i) regioisomers formed by adding these radicals to carbon atoms of the *cis-n* bonds and (ii) SAs formed by adding the radicals to carbon atoms of other bonds in complexes **1**—**3**. The hyperfine structure of the EPR spectrum essentially depends on the spatial structure of substituents at the metal atom and allows individual regioisomers of not only phosphoryl radicals, but also carbon-centered radicals R^2 and R^3 with metallofullerenes **1**—**3** to be identified. The rate constants for addition of R^2 and R^3 radicals to complexes **2** and **3** were determined.

Key words: metallofullerenes; EPR spectroscopy; steric and electronic effects; phosphoryl, *tert*-butyl, and trichloromethyl radicals; regioselectivity; rate constants for addition.

Recently, C_{60} fullerene derivatives have been widely and successively used in chemistry and biology.**[1]** Unlike centrosymmetric C_{60} fullerene, attachment of various groups leads to deformation of the carbon cages of its derivatives and appearance of nonequivalent chemical bonds, such as *cis-n*, *e-,* or *trans-n* (*n* = 1, 2, 3, 4). As a result, particular carbon atoms involved in these bonds (Fig. 1) show different reactivities toward free radicals, which results in a variety of different regioisomers. The reactivity and regioselectivity of the addition of free radicals to C_{60} fullerene derivatives depends on at least four factors. These are (1) pyramidality of carbon atoms of particular bonds due to deformation of the fullerene cage (pyramidality is characterized by the sum of the bond angles at a carbon atom and affects only the *cis*-bonds and does not affect the *e*- and *trans*-bonds); 2) steric properties of substituents that can shield the carbon atoms of the *cis-n* bonds (*n* = 1, 2, 3) and thus prevent free radicals from being added to these atoms; 3) donor-acceptor properties of the metallofragment or organic group attached to fullerene, because they can affect the regioselectivity of addition of free radicals and the stability of spin adducts (SAs) formed; and 4) steric and polar properties of the radical that adds.

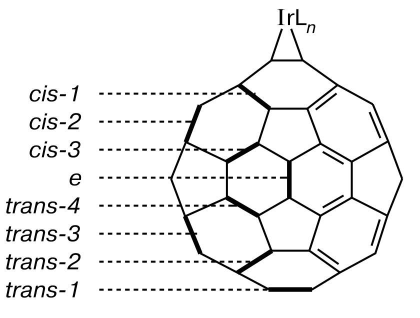

Fig. 1. Reaction centers in C_{60} fullerene derivatives.

It is not improbable that all these factors determining the reactivity and regioselectivity of addition of radicals to fullerene derivatives will most clearly manifest themselves in the case of metal complexes of fullerenes, because, unlike methano- and pyrrolidinofullerenes, the metallofragment can have a strong electronic effect on adjacent carbon atoms and produce steric hindrances due to the ligands bonded to the metal atom.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1302—1309, July, 2007.

In this connection, in the present work we carried out an EPR study of the addition of $^{\bullet}P(O)(OPr^i)_2$ (R^1), $^{\bullet}CMe_3$ (R^2), and $^{\bullet}CCl_3$ (R^3) radicals differing in electronic properties and size to complexes $(\eta^2\text{-}C_{60})IrH(CO)(CNBu^t)_2(o\text{-}HCB_{10}H_9CCH_2PPh_2\text{-}B,P)$ (**1**), $(\eta^2\text{-}C_{60})IrH(CO)(DIOP)$ (DIOP is (4*R*,5*R*)-(+)-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane, **2**), and $(\eta^2\text{-}C_{60})IrH(CO)(PPh_3)_2$ (**3**). These complexes were chosen for the following reasons. First, the metal atom (Ir) coordinates ligands possessing different electron donor and electron-withdrawing abilities; this can affect the degree of charge transfer from the Ir atom to fullerene. Second, phenyl rings in the iridium complexes of C_{60} fullerene can approach the fullerene surface, arrange parallel to the hexagonal faces, and thus preclude the addition of free radicals to carbon atoms of the bonds near the metallofragment.[2]

The EPR spectra recorded[3—7] upon addition of R^1 radicals to fullerene derivatives (in particular, complex **3**,[4] methano-,[6] or pyrrolidinofullerenes[7]) exhibit signals of several regioisomeric SAs. X-ray analysis data and results of theoretical calculations[6,7] suggest that the R^1 radicals mainly attack carbon atoms of the *cis-n* bonds of methanofullerenes or pyrrolidinofullerenes, because these atoms are characterized by the highest pyramidality. However, no signal assignment to particular regioisomers was done, because signals in the EPR spectra of all regioisomers showed identical, low stability and rapidly disappeared due to recombination when illumination was switched off, although the stability of individual regioisomers should depend on the mutual position of the substituent in the fullerene derivative molecule and the radical attached, which in turn is determined to which carbon atoms of the *cis-n*, *e-*, or *trans-n* (n = 1, 2, 3, 4) bonds does the addition of radicals occur. EPR studies of the addition of carbon-centered radicals to C_{60} fullerene derivatives mainly revealed singlet signals.[6,7] Although these singlets were relatively stable, structureless EPR spectra made impossible to obtain information on the regioselectivity of addition and, therefore, to assess the reactivity of carbon atoms of particular *cis-n*, *e-* or *trans-n* bonds.

Experimental

EPR spectra were recorded on a Varian E-12A spectrometer. Deaerated reaction mixtures placed in glass tubes were irradiated with a DRSh-1000 lamp in the spectrometer cavity at ~20 °C. The 366-nm and 640-nm bands were cut using glass light filters. The *g*-factors of the radicals under study were calculated using a Varian pitch (g = 2.0028) as a reference. Kinetic data were processed with the Microsoft Excel program. The correlation coefficients were at least 0.9. The error in determination of the addition rate of free radicals (see text) was ±20% for three runs.

The R^1 radicals were generated by photochemical decomposition of $\{Hg[OP(OPr^i)_2]_2\}$ (**4**) ((5—10) $\cdot$ 10^{-3} mol L^{-1}) and the R^2 (R^3) radicals were produced by abstracting Br (Cl) atoms from $BrCMe_3$ (0.1—0.3 mol L^{-1}) or CCl_4 (0.2—0.4 mol L^{-1}) molecules by $^{\bullet}Re(CO)_5$ radicals formed in the photochemical decomposition of $Re_2(CO)_{10}$ ((0.5—1) $\cdot$ 10^{-3} mol L^{-1}).[8] Metallofullerenes (10^{-3} mol L^{-1}) were synthesized following known procedures[9—11] using 2,3,5,6-Me_4C_6HNO (ND), 2,4,6-$Bu^t_3C_6H_2NO$ (BNB) (Sigma), and *N-tert*-butyl-α-phenylnitrone (PBN) (Aldrich) as spin traps. The spin trap and metallofullerene concentrations lower than 10^{-3} mol L^{-1} were obtained by successive dilution.

Quantum chemical calculations of complexes **1** and **2** were carried out by the density functional theory in the pseudopotential approximation with the exchange-corrlation functiional (DFT-PBE)[12] using the PRIRODA program.[13]

Results and Discussion

Addition of R^1 radicals to fullerene metal complexes 1—3. EPR spectra of benzene solutions containing compound **1** and **4** irradiated with unfiltered light of the mercury lamp exhibit signals of six regioisomers (Table 1). As the lamp is switched off, signals of three SAs are mainly observed in the spectra for a long time.

Such a great stability difference between the SAs formed suggests that only stable regioisomers can be detected when R^1 radicals are generated under milder conditions. Indeed, in studying the addition of the R^1 radicals

Table 1. Magnetic-resonance parameters of EPR spectra of spin adducts of R^1 radicals with metallofullerenes **1**—**3**

Metallo-fullerene	Initiation technique	a_P/G	g-Factor
1	Illumination with unfiltered light of mercury lamp	65.7	2.0055
		61.2	2.0055
		58.0	2.0049
		54.2	2.0049
		48.7	2.0051
		44.0	2.0054
	366-nm light	65.7	2.0055
		58.0	2.0049
		44.0	2.0054
2	Illumination with unfiltered light of mercury lamp	63.2	2.0059
		62.5	2.0043
		62.5	2.0029
		61.5	2.0022
		52.5	2.0059
	366-nm light	63.2	2.0059
		52.5	2.0059
3	Illumination with unfiltered light of mercury lamp	70.0	2.0023
		67.0	2.0030
		65.0	2.0028
		63.5	2.0023
		60.0	2.0023
		58.5	2.0025

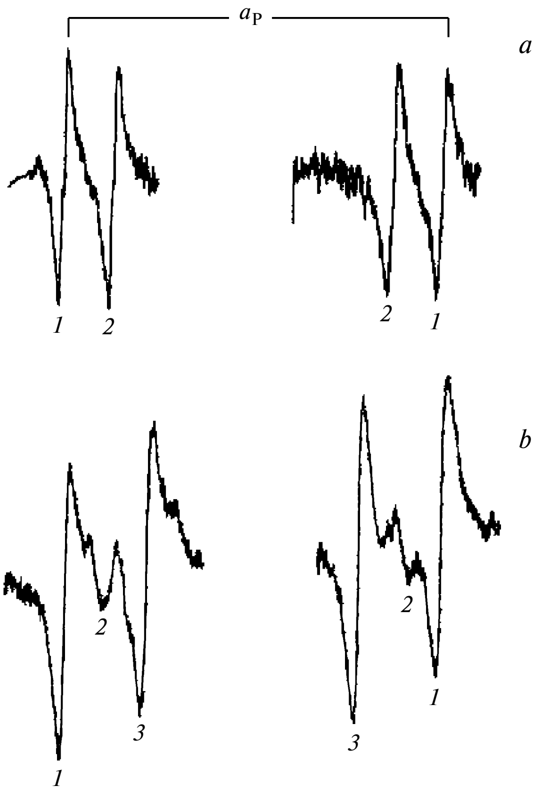

Fig. 2. EPR spectra of radicals generated upon illumination of toluene solutions of complex **4** and metallofullerene **2** (*a*) or **1** (*b*) with 366-nm light. Figures "*1*", "*2*", and "*3*" denote signals of different regioisomers.

generated with 366-nm light to complex **1** we were able to distinguish between the more and less stable radicals (Fig. 2, *b*, see Table 1). The EPR spectrum mainly exhibits signals of three regioisomers, of which two give the most intense signals (see Fig. 2, *b*). Spin adducts of the R^1 radical with complex **1** are significantly different from those of the SAs of metallofullerenes,[3,4] methanofullerenes, and pyrrolidinofullerenes[6,7] in properties and magnetic-resonance parameters. As illumination is switched off, the signal intensities of the regioisomers of SAs of R^1 radicals with complex **1** become nearly halved over a period of about 40 min. The intensities of all three signals decrease at nearly equal rates, whereas the signals of the SAs of other fullerene derivatives with the R^1 radicals disappear just after switching off irradiation. The regioisomers formed are characterized by a large positive shift of the *g*-factor relative to those of $^{\bullet}C_{60}R^1$ (g = 2.0023) and of SAs of R^1 radical with other C_{60} derivatives. In addition, the HFC constants a_P of the regioisomers formed are much lower than the corresponding HFC constants of $^{\bullet}C_{60}R^1$ and of the SAs of R^1 radicals with complex **3** (see below), methanofullerenes,[6] and pyrrolidinofullerenes.[7] It follows that the R^1 radicals add to carbon atoms of that hemisphere of complex **1** to which the metallofragment is attached, namely, to carbon atoms of the *cis-n* bonds because only in this case the SAs formed can differ from the SAs of the R^1 radical with C_{60} and other fullerene derivatives in magnetic-resonance parameters. This type of regioselectivity of the addition of R^1 radical to complex **1** is most likely due to an increase in the electron density on fullerene owing to the donor ability of the metallofragment. This electron density is localized near the metallofragment.

The pyramidality differences between carbon atoms participating in the *cis-1* (347.2°), *cis-2* (347.2°), and *cis-3* bonds (346.2—346.6°) lie within the limits of experimental error of X-ray analysis and therefore it is impossible to decide between two alternatives only based on the value of this parameter. However, the pyramidality of carbon atoms is not the exclusive factor affecting their reactivity in the addition of R^1 radicals.

The SA stability also depends on the steric properties and polarity of the metallofragment and the radical being added. A similar pattern of fullerene cage deformation is also known for organic derivatives of C_{60} fullerene.[6,7] Based on the structures of organic C_{60} derivatives (see Refs 6 and 7), the atoms involved in the *cis-n* bond in SAs should be unshielded, which is the reason for ready recombination of these species. In addition, since organic fragments can only weakly interact with the radical centers of SAs, their magnetic-resonance parameters are strongly different from those of the SAs of the R^1 radical with complex **1**. Analysis of the structure of complex **1** and the stability and magnetic-resonance parameters of the SAs with R^1 one radicals suggest that three stable signals observed in the EPR spectrum should be attributed to the *cis-1* and *cis-2* isomers rather than *cis-3* one because the *cis-3* positions are not shielded. Contrary to this, in the case of addition of the R^1 radical to carbon atoms in the *cis-1* and *cis-2* positions the radical centers of SAs are sterically shielded due to the close proximity of the radical attached and the ligands at the metal atom. Therefore, bimolecular recombination reactions of these SAs are improbable. It is likely that steric hindrances are first of all produced by the PPh_2 group of the ligand in complex **1**. Regioselectivity of the addition is also indicated by the significant HFC constant and *g*-factor difference between the SAs of the R^1 radical with complex **1** (see Table 1) and the SAs formed by C_{60} fullerene (a_P = 63.25 G, g = 2.0023) and its derivatives.[3—7] Probably, the singlet with a_P = 44.5 Gs characterizes the SA formed upon addition of the R^1 radical to carbon atoms of the *cis-1* bonds located on the other side relative to the PPh_2 group and is not sterically shielded by this group while the other two signals appear upon addition of the R^1 radical to the *cis-2* bonds.

Three more SAs are detected in the EPR spectra of solutions containing complexes **1** and **4** and irradiated with unfiltered light of the mercury lamp, but they do not appear upon illumination with 366-nm light. This is due to the fact that they are formed by adding the R^1 radical to carbon atoms of other, more distant bonds in complex **1**. Therefore, such SAs readily recombine to form dimers and irradiation with 366-nm light causes no dissociation of these species. Based on the magnetic-resonance parameters of these SAs, one can assume that they are formed *via* addition of R^1 radicals to the *cis*-3- and/or *e*-bonds. Would their formation involve the addition of the R^1 radical to the *trans-n* bonds, the parameters of such SAs would be similar to those of the SAs of the R^1 radical with C_{60} (a_P = 63.25 G, g = 2.0023), which is not observed in this case.

Figure 2, *a* presents the EPR spectrum recorded during irradiation of toluene solutions of complexes **2** and **4** with 366-nm light. Table 1 lists the magnetic-resonance parameters of the SAs detected. From Fig. 2 it follows that addition of the R^1 radical to complex **2** results in two regioisomers. Comparison of the HFS and the a_P values and g-factors with the corresponding parameters of the SAs of the R^1 radical with complex **1** shows that the presence of DIOP only causes the HFS to change. As illumination is switched off, the signals of the SAs of the R^1 radicals with complex **2** retain their intensities for nearly 15 min. Thus, in this case the R^1 radical also adds to the fullerene hemisphere to which the metallofragment is attached. Probably, this is due to the donor ability of this fragment, whereas the ligands at the metal atom are responsible for the regioselectivity of addition. Unlike the ligands in complex **1**, the "rigid" seven-membered ring causes such a mutual arrangement of the Ph rings at two P atoms (one of them is in equatorial plane and the other occupies an axial positron in the octahedral coordination sphere of the iridium atom) with respect to the carbon atoms of the *cis-n* bonds that they sterically shield the addition of R^1 radicals to the carbon atoms of the *cis-1* bonds near the ligands bonded to the metal atom. The attack of R^1 radicals on the carbon atoms of the *cis-2* bonds follows from the stability of the SAs formed, the decrease in the a_P HFC constant, and an increase in the g-factor value (see Table 1), which indicates a high degree of delocalization of the unpaired electron directed to the metallofragment. Theoretical calculations of complex **2** revealed the highest pyramidality for the atoms of the *cis-n* bonds while from analysis of the Mulliken effective charge distribution it follows that the Ir atom has a positive charge similar to unity, whereas the fullerene fragment bears an equal (in absolute value) negative charge (Fig. 3), which is mainly concentrated on the carbon atoms of the double bonds in the nearest environment of the Ir atom.

The other three SAs manifest themselves in the EPR spectrum when the solutions containing complexes **2** and **4** are illuminated with unfiltered light of the mercury lamp; however, they remain "EPR silent" when the solution is irradiated with 366-nm light. This reasons may be the same as in the case of the reactions of complexes **1** and **4**.

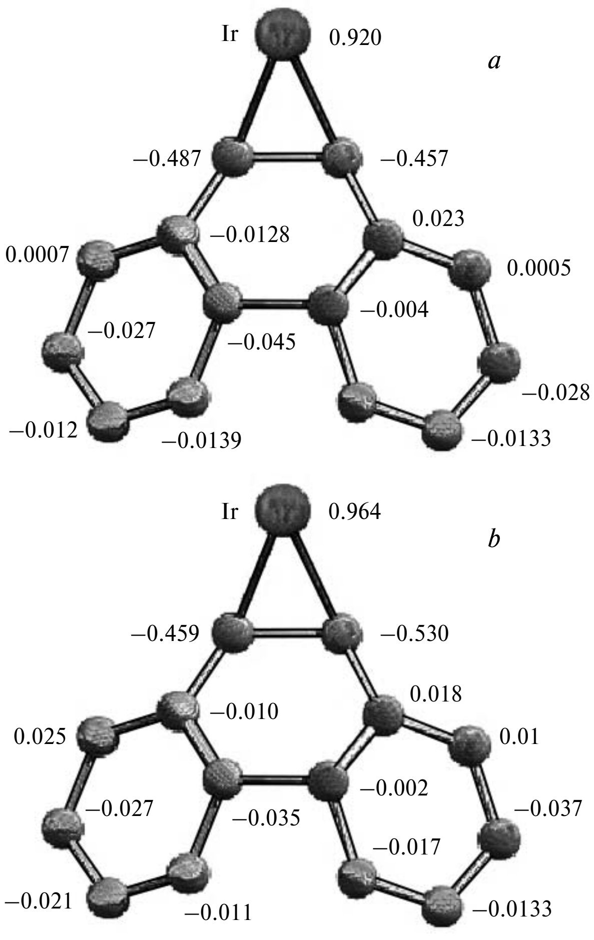

Fig. 3. Effective charge distribution on Ir and C atoms in complexes **3** (*a*) and **2** (*b*).

Based on the magnetic-resonance parameters of one SA (a_P = 62.5 G, g = 2.0043), one can assume that this SA is formed due to the addition of the R^1 radical to the *cis-3-* and/or *e*-bonds. The other two SAs are likely formed by adding the R^1 radical to the *trans-n* bonds, because their parameters are similar to those of the SAs of the R^1 radical with C_{60} (a_P = 63.25 G, g = 2.0023).

The EPR spectra of the toluene solutions of complexes **3** and **4** illuminated with unfiltered light of the mercury lamp exhibit signals of six regioisomers (see Table 1); the longer the irradiation time the more intense the doublet characterized by a_P = 63.5 G and g = 2.0023.[4] With allowance for these data and based on equality of the magnetic-resonance parameters with the corresponding parameters of the SAs of the R^1 radical with C_{60}, it was assumed[4] that these radicals are formed as a result of light-assisted demetallation of complex **3** resulting in C_{60} fullerene to which the R^1 radical is then added. Since no doublet characterized by a_P = 63.5 G and g = 2.0023 was detected in the reactions of complex **4** with other iridium complexes, we decided to assess the possibility of demetallation of complex **3**.

To study (possible) demetallation of complex **3** illuminated with unfiltered light of the mercury lamp, benzene solutions of complex **3** in glass tubes were preliminarily irradiated using a PRK-2 lamp for 2 h. After adding necessary amounts of complex **4** and degassing the tubes the reaction mixtures were illuminated with unfiltered light of the DRSh-1000 lamp for 30—40 min in the spectrometer cavity. The EPR spectra again exhibited signals of six regioisomers, but the intensity of the doublet with a_P = 63.5 G and g = 2.0023 in the preliminarily irradiated sample did not increase considerably compared to the untreated sample. This indicates that no significant demetallation of complex **3** occurs under the conditions of our experiments. Therefore, the doublet characterized by these parameters should be attributed to SAs of those regioisomers that are formed in the addition of the R^1 radical to carbon atoms of the *cis-3*, *e-*, or *trans-n* bonds. This is consistent with the fact that the doublet with a_P = 63.5 G and g = 2.0023 is also observed when the R^1 radical is added to methano-[**6**] and pyrrolidinofullerenes,[**7**] although these compounds are known to be stable. In addition, in both cases the signals of this doublet and other doublets disappear in a few seconds as illumination is switched off.

The results of the experiments on generation of R^1 radicals under milder conditions using illumination with 366-nm light confirm that complex **3** does not undergo demetallation. No SA formation in the reactions of complexes **3** and **4** initiated with 366-nm light was detected. One can assume that SAs recombine faster than emerge under these conditions. Indeed, when the reaction mixtures were again illuminated with 640-nm light (in this case dimeric SAs should decompose[**5**] but no generation of phosphoryl radicals from complex **4** occurs), the EPR spectrum showed signals of six regioisomers. Their parameters match the magnetic-resonance parameters (see Table 1) reported in a study[**4**] where radicals were generated by irradiating with unfiltered light of the mercury lamp. It follows that manifestation of regioisomeric SAs of R^1 radicals with complex **3** in EPR spectra during illumination of reaction mixtures with unfiltered light of the mercury lamp (in contrast to experiments with 366-nm light) is due to not only an increase in the generation rate of the R^1 radical but also decomposition of dimers that are formed as a result of recombination of SAs illuminated with 640-nm light.

The results obtained show that the R^1 radical adds to carbon atoms of the bonds that are far from the metallofragment. Only in this case the ligands at the Ir atom do not preclude dimerization of the SAs formed. This is also indicated by the fact that the g-factors of these SAs are equal to those of SAs formed by other C_{60} derivatives,[**6,7**] *i.e.*, the metallofragment has no effect on the magnetic-resonance parameters of regioisomers. However, our calculations of complex **3** showed that the Ir atom bears a positive charge similar to unity while the fullerene sphere has a negative charge mainly localized on carbon atoms of the double bonds adjacent to the Ir atom (see Fig. 3, *a*). Therefore, one would expect the addition of electrophilic radical R^1 to carbon atoms of the *cis-1* or *cis-2* bonds.

Based on these data, one can assume that two PPh_3 groups sterically shield carbon atoms of the bonds near the substituent, *e.g.*, the *cis-1* and *cis-2* bonds. This is confirmed in the course of geometry optimization of the most stable structure **3** using quantum chemical calculations, according to which phenyl groups at the P atoms produce steric hindrances to the addition of R^1 radicals to carbon atoms of the *cis-1* and *cis-2* bonds.

These data prove that all regioisomeric SAs are formed in the addition of R^1 radical to carbon atoms of the *cis-3*, *e-*, or *trans-n* bonds of the metal complex **3**.

Thus, the results obtained show that, depending on the initiation technique, the EPR spectra exhibit signals of different regioisomers of SAs of R^1 radicals with fullerene metal complexes **1**—**3**. Illumination of metallofullerenes **1** and **2** with 366-nm light causes the formation of mainly stable regioisomers, *cis-1* and *cis-2*, in which the ligands at the metal atom and the attached radical R^1 sterically shield the radical centers on the carbon atoms of the *cis-1* or *cis-2* bonds and recombination of these species is difficult. It also follows that phenyl groups at the ligand phosphorus atom produce severe steric hindrances to carbon atoms of the *cis-1* and *cis-2* bonds, attack on R^1 radicals.

Addition of R^2 and R^3 radicals to metallofullerenes 1—3. The addition of R^2 radicals generated with 366-nm light to complexes **1**, **2**, or **3** causes the appearance of singlet signals of various regioisomers in the EPR spectrum (Table 2). It is known that the addition of carbon-centered radicals to methano- or pyrrolidinofullerenes C_{60} is characterized by asymmetric structureless singlet signal in the EPR spectra. The observed differences between the EPR spectra of the SAs of the R^2 and R^3 radicals with complexes **1**—**3** are likely due to the presence of the metallofragment. Electronic effects of the metal atom and substituents at this atom cause significant delocalization of the electron density in the SAs formed and favor changes in the g-factors; this makes it possible to detect singlet signals of particular regioisomers (Fig. 4, *a*, *c*). The effect of the metallofragment should depend on the distance to the radical center. With allowance of the g-factor values, we assigned the singlets in the regions g = 2.0071—2.0084 and 2.0034—2.0056 to regioisomers formed in the addition of R^2 radicals to carbon atoms of the *cis-1* and *cis-2* bonds, respectively. The other two singlets in the region g = 2.0024—2.0027 (for one of them the g-factor is equal to that of SAs of R^2 radicals with C_{60}[5]) were assigned to regioisomers formed by the addition of R^2 radicals to carbon atoms of bonds located far from the substituent (as a consequence, the metallofragment does not

Table 2. *g*-Factors of regioisomers of R^2 and R^3 radicals with metallofullerenes **1—3** (illuminatio with 366-nm light)

Radical	*g*-Factor*	Assignment
$^{\bullet}\mathbf{1}\cdot R^2$	$g_1 = 2.0084$	*cis-1*
	$g_2 = 2.0056$	*cis-2*
	$g_3 > g_4$	
	$g_4 > g_5$	
	$g_5 = 2.0024$	*cis-3*, *e*, *trans-n*
$^{\bullet}\mathbf{1}\cdot R^3$	$g_1 = 2.0096$	*cis-1*
	$g_2 = 2.0073$	*cis-1*
	$g_3 = 2.0038$	*cis-3*, *e*, *trans-n*
$^{\bullet}\mathbf{2}\cdot R^2$	$g_1 = 2.0071$	*cis-1*
	$g_2 = 2.0034$	*cis-3*
	$g_3 = 2.0024$	*cis-3*, *e*, *trans-n*
$^{\bullet}\mathbf{2}\cdot R^3$	$g_1 = 2.0094$	*cis-1*
	$g_2 = 2.0061$	*cis-1*
	$g_3 = 2.0056$	*cis-2*
	$g_4 = 2.0047$	*cis-2.*
	$g_5 = 2.0041$	*cis-3*
	$g_6 = 2.0034$	*cis-3*, *e*, *trans-n*
$^{\bullet}\mathbf{3}\cdot R^2$	$g_1 = -2.0077$	*cis-1*
	$g_2 = -2.0072$	*cis-1*
	$g_3 = 2.0049$	*cis-2*
	$g_4 = 2.0044$	*cis-2*
	$g_5 = 2.0025$	*cis-3*, *e*, *trans-n*
	$g_6 = 2.0022$	*cis-3*, *e*, *trans-n*
$^{\bullet}\mathbf{3}\cdot R^3$	$g_1 = 2.0093$	*cis-1*
	$g_2 = 2.0064$	*cis-1*
	$g_3 = 2.0056$	*cis-2*
	$g_4 = 2.0044$	*cis-2.*
	$g_5 \approx 2.0032$	*cis-3*, *e*, *trans-n*

* Calculated using simulated spectra.

affect the radical center). The mutual position of the metallofragment and the R^2 radical in SAs will shield the radical center and thus hamper bimolecular reactions of SAs. The shorter the distance between the metallofragment and the radical center the slower the recombination of radicals. Comparison of Fig. 4, *a* and Fig. 4, *b* shows that in the region $g = 2.0025—2.0027$ the signals of the regioisomers of $\mathbf{3}\cdot R^2$ radicals weaken much faster than signals of other regioisomers, which is consistent with signal assignment to individual regioisomers (see above). Similar results concerning stabilities of regioisomers were also obtained taking compounds **2** and **1** as examples.

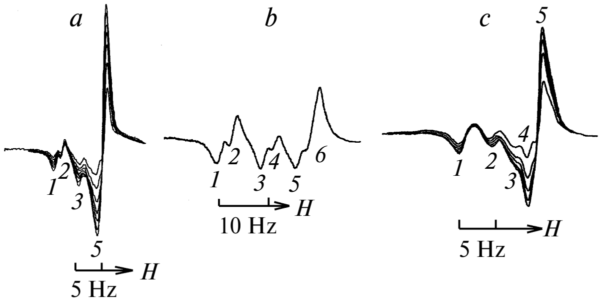

Fig. 4. EPR spectra of radicals generated upon illumination of toluene solutions of a mixture of $Re_2(CO)_{10}$, $BrCMe_3$, and metallofullerene **3** (*a*, *b*) or metallofullerene **1** (*c*) with 366-nm light. The spectra were recorded with 40 s time intervals, spectrum *b* — 80 min after switching the light off. Figures "*1*", "*2*", "*3*", "*4*", "*5*", and "*6*" denote the signals of different regioisomers.

The addition of R^3 radicals to complex **1**, **2** or **3** causes the appearance of singlet signals of several regioisomers in the EPR spectra (see Table 2, Fig. 5).

Taking into account the electronic effects of the metallofragment, we assigned the singlet signals in the region $g = 2.0094—2.0097$ and $2.0051—2.0073$ to regioisomers formed in the addition of R^3 radicals to carbon atoms of the *cis-1* and *cis-2* bonds. Singlets in the region $g = 2.0042—2.0035$ seems to appear when the R^3 radicals add to carbon atoms of the bonds that are far from the metallofragment, because one of the *g*-factors is equal to that of SAs of R^3 radicals with C_{60}.[5] The assignment made is also confirmed by the results of a study of the stability of regioisomers. For instance, the signal intensities of the *cis-1* and *cis-2* regioisomers remain unchanged for a period of 12 min after switching off illumination, whereas the signal intensities of other regioisomers become nearly halved. We have no quantitative data on the stabilities of individual regioisomers of the SAs of R^3 radicals with fullerene derivatives. Probably, the regioisomers whose signals weaken somewhat faster compared to the signals of other isomers are formed in the addition of R^3 radicals to carbon atoms of fullerene hemisphere of compound **2** containing no substituents, *i.e.*, to carbon atoms of the *e* and *trans* bonds.

Thus, we for the first time identified regioisomers of SAs of the R^2 and R^3 radicals with complexes **1—3** by EPR spectroscopy. The results obtained make it possible to determine the reactivities of carbon atoms of individual bonds in these compounds toward carbon-centered radicals, which is necessary for further use of the complexes in question in chemical reactions.

Rate constants for addition of R^2 and R^3 radicals to metallofullerenes 2 and 3. The rate constants for addition

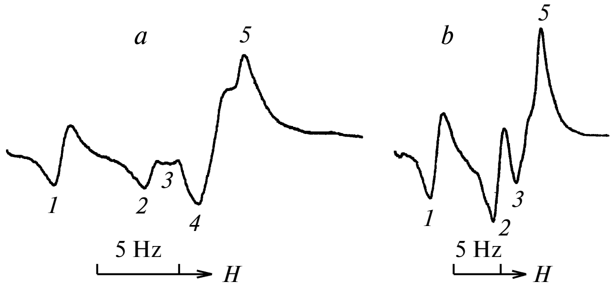

Fig. 5. EPR spectra of radicals generated upon illumination of toluene solutions of a mixture of $Re_2(CO)_{10}$, CCl_4, and metallofullerene **3** (*a*) or **2** (*b*) with 366-nm light. Figures "*1*", "*2*", "*3*", "*4*", and "*5*" denote the signals of different regioisomers.

of R^2 and R^3 radicals to compounds L_nIrC_{60} (L_nIrC_{60} are complexes **2** and **3**) were determined using the kinetics of competing reactions (Eqs (1) and (2)).

$$R^2 + L_nIrC_{60} \xrightarrow{k_1} \underset{\mathbf{A}}{L_nIr^{\cdot}C_{60}R^2} \qquad (1)$$

$$R^3 + L_nIrC_{60} \xrightarrow{k_2} \underset{\mathbf{B}}{L_nIr^{\cdot}C_{60}R^3} \qquad (2)$$

The competing reactions were as follows: the addition of R^3 radicals to PBN

$$R^3 + PhCH{=}N(O)CMe_3 \xrightarrow{k_3}$$
$$\longrightarrow \underset{\mathbf{C}}{PhCHR^3N(^{\cdot}O)CMe_3}, \qquad (3)$$

and the addition of R^2 radicals to ND or BNB

$$R^2 + 2,3,5,6\text{-}Me_4C_6HNO \xrightarrow{k_4}$$
$$\longrightarrow \underset{\mathbf{D}}{2,3,5,6\text{-}Me_4C_6H\ N(^{\cdot}O)R^2} \qquad (4)$$

$$R^2 + 2,4,6\text{-}Bu^t{}_3C_6H_2NO \xrightarrow{k_5}$$
$$\longrightarrow \underset{\mathbf{E}}{2,4,6\text{-}Bu^t{}_3C_6H_2{}^{\cdot}NOR^2}. \qquad (5)$$

Figure 6 presents the EPR spectrum of radicals generated upon irradiation of toluene solutions of a mixture containing PBN ($2.7 \cdot 10^{-2}$ mol L^{-1}), compound **2** ($2 \cdot 10^{-4}$ mol L^{-1}), CCl_4, and $Re_2(CO)_{10}$ (10^{-3} mol L^{-1}. The spectrum exhibits the previously reported[14] signals of SAs of the R^3 radicals with PBN (triplet of doublets with $a_N = 13.6$ and $a_H = 1.6$ G) and singlet signals ($g = 2.0094$, 2.0041, and 2.0034) of regioisomers with complex **2**. The signals of the SAs of the R^3 radicals with PBN and the singlet with $g = 2.0094$ have identical stabilities. Similar results were also obtained taking compound **3** as an example. Having measured the accumulation rates of the SAs of the R^3 radicals with PBN ($d\mathbf{C}/dt = 5$) and the regioisomers ($g = 2.0093$ and 2.0094) of compounds **3** and **2** ($d\mathbf{B}/dt = 26$) (see Experimental) with allowance for the signal multiplicities and linewidths ($\Delta H = 1.1$ and 1.8 G) and assuming a value of $7 \cdot 10^4$ L mol^{-1} s^{-1} for the rate constant for addition of the R^3 radicals to PBN,[15] the rate constant for addition of the R^3 radicals to carbon atoms of the *cis-1* bond in complexes **3** and **2** was estimated at 10^7 L mol^{-1} s^{-1}. The EPR spectrum of compound **2** (see Fig. 5, *b*), the stabilities and accumulation rates (see Table 2) of the regioisomers, and the linewidths suggest that the rate constants for addition of radicals to carbon atoms of the *cis-2* bond will be of the same order of magnitude. Taking into account the fact that C_{60} fullerene has a total of sixty equivalent carbon atoms to which the R^3 radicals can add and that the rate constant for addition of the R^3 radicals to C_{60} is 10^8 L mol^{-1} s^{-1},[16] it follows that the electronic effect of the metallofragment enhances the reactivities of the carbon atoms of the *cis-1* and *cis-2* bonds in complexes **3** and **2** toward the R^3 radicals by nearly an order of magnitude.

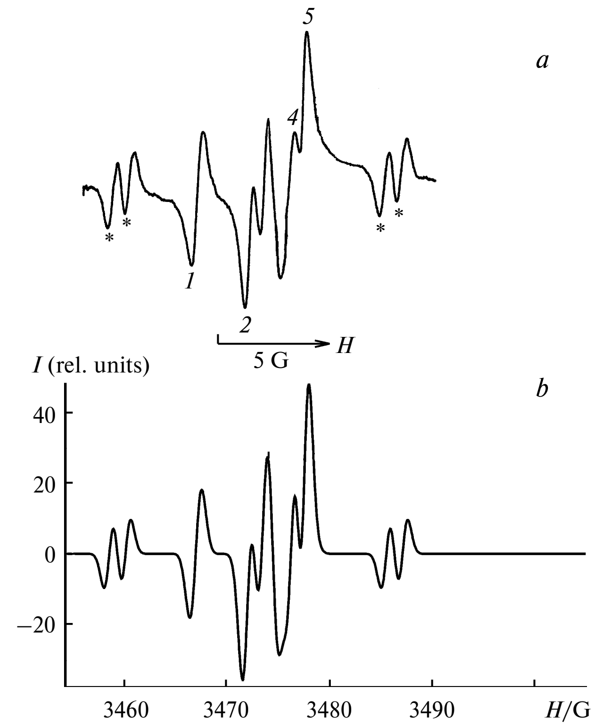

Fig. 6. Experimental (*a*) and simulated spectra (*b*) EPR spectra of radicals generated upon illumination of toluene solutions of a mixture containing metallofullerene **2** ($2 \cdot 10^{-4}$ mol L^{-1}), PBN ($2.7 \cdot 10^{-2}$ mol L^{-1}), $Re_2(CO)_{10}$, and CCl_4 with 366-nm light. For the signal numbering scheme, see Fig. 5. The signals of the SAs of CCl_3 radicals with PBN are asterisked.

The EPR spectra of irradiated toluene solutions containing ND (10^{-4} mol L^{-1}), compound **2** (10^{-3} mol L^{-1}), $Re_2(CO)_{10}$, and $BrCMe_3$ show signals of the known[17] SAs of R^2 radicals with ND ($a_N = 14.2$ G, $g = 2.006$). Having measured the rate of formation of the SAs of the R^2 radicals with **2** ($d\mathbf{A}/dt = 1$), for the regioisomer with $g = 2.0071$ (see Table 2) and ND ($d\mathbf{D}/dt = 3.9$ with allowance for spectral multiplicity and linewidths) and assuming a value of $2 \cdot 10^8$ mol L^{-1} s^{-1} for the rate constant for addition of the R^2 radicals to ND,[15] the rate constant for addition of the R^2 radicals to carbon atoms of the bonds in the *cis*-isomer of compounds **2** was estimated at about 10^6 mol L^{-1} s^{-1}. In addition, based on the overall rate of formation of regioisomers (see Fig. 5, *b*, signals *2* and *3*, $d\mathbf{A}/dt = 9.2$ with allowance for linewidth and multiplicity of the radicals), the rate constants for addition of the R^2 radicals to carbon atoms of the *cis-3*, *e*, and *trans* bonds was estimated at ~10^7 mol L^{-1} s^{-1}, which is similar to the rate constant for addition of the R^2 radicals to C_{60} fullerene.[18] This again confirms correctness of our assign-

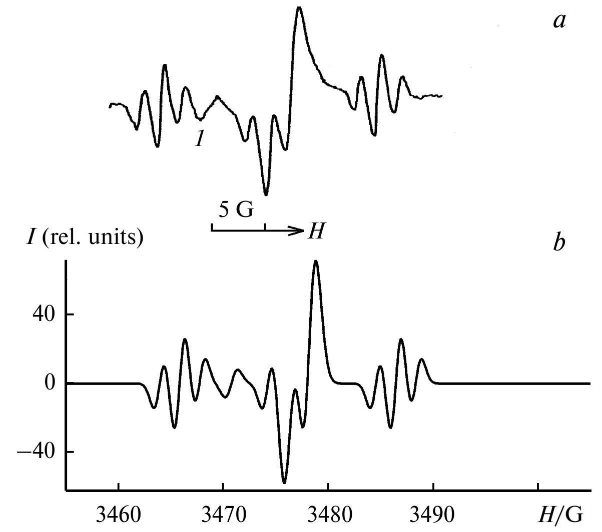

Fig. 7. Experimental (*a*) and simulated (*b*) EPR spectra of radicals generated by illumination of toluene solutions of a mixture of metallofullerene **2** (10^{-3} mol L^{-1}), BNB ($2.6 \cdot 10^{-3}$ mol L^{-1}), $Re_2(CO)_{10}$, and $BrCMe_3$ with 366-nm light. Figure "*1*" denotes the signal of a regioisomer.

ment of individual signals to certain regioisomers that are formed in the addition of the R^2 radicals to metallofullerenes.

Figure 7 shows the EPR spectrum recorded during irradiation of toluene solutions of a mixture of BNB ($2.6 \cdot 10^{-3}$ mol L^{-1}), **2** (10^{-3} mol L^{-1}), $Re_2(CO)_{10}$, and $BrCMe_3$. The EPR spectrum shows signals of the known[19] SAs of the R^2 radicals with BNB ($a_N = 10.3$, $a_{m\text{-H}} = 1.9$ G, $g = 2.004$) and the regioisomer with $g_1 = 2.0071$. Having measured the rate of formation of the SAs of R^2 radicals with complex **2** (see Fig. 7, signal *1*, $d\mathbf{A}/dt = 2$) and BNB ($d\mathbf{E}/dt = 3.9$) and assuming the rate constant for addition of the R^2 radicals to BNB equal to $2 \cdot 10^6$ mol L^{-1} s^{-1},[15] with allowance for the spectral multiplicity and linewidths the rate constant for addition of the R^2 radicals to carbon atoms of the bonds in *cis*-isomers of compound **2** was estimated at about 10^6 mol L^{-1} s^{-1}. Comparison of the rate constants for addition of the R^2 and R^3 radicals to compounds **3** and **2** shows that electrophilic radical R^3 is an order of magnitude more reactive than the R^2 radicals toward the addition to these compounds, although they have identical spatial structures. This is consistent with the results of calculations of charge redistribution on the fullerene fragment and the metal atom (see above).

This work was financially supported by the Federal Agency on Science and Innovations of the Ministry of Education and Science of the Russian Federation (Contracts Nos 02.513.11.3207 and 02.513.11.3209) and by the Russian Foundation for Basic Research (Project No. 03-03-32695).

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Received January 23, 2007;
in revised form March 22, 2007