Spin-adducts of η^2-metallocomplexes of fullerene-60 with phosphoryl radicals

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Using ESR spectroscopy, the reaction of $^{\cdot}P(O)(OPr^i)_2$ phosphoryl radicals with $C_{60}ML_2$ (M = Pd, Pt) was studied and the spin-adducts formed were shown to be unstable under the reaction conditions. The η^2-addition of $Pt(PPh_3)_4$ to the dimer of phosphoryl-fullerenyl radicals results in metal-containing dimers $(RO)_2(O)PL_2MC_{60}{-}C_{60}ML_2P(O)(OR)_2$, which dissociate when exposed to visible light to afford $^{\cdot}C_{60}ML_2P(O)(OR)_2$ radicals; ML_2 in these complexes is located in different positions in relation to the radical center. As a result, the ESR spectra contain the superposition of at least five signals of radicals that differ in HFS constants and *g*-factors.

Key words: fullerene, metal; radical, phosphoryl; ESR spectra.

Free radicals with an unpaired electron at C, P, B, S and other atoms add to double bonds of fullerenes to form spin-adducts observable by ESR spectroscopy.[1—8] It has been found that mono-adducts of fullerenyl radicals dimerize reversibly,[4,6] and the products of addition of several radicals are relatively stable.[2,6] It is possible to draw conclusions about the structure of paramagnetic adducts of several radicals based on the hyperfine splitting (HFS) constants of the unpaired electron with the magnetic nuclei of the added radicals. It has been shown previously[2] that the addition of five benzyl radicals to fullerene C_{60} proceeds regioselectively with the formation of the allyl radical, $^{\cdot}C_{60}(CH_2Ph)_3$, and then the cyclopentadienyl radical, $^{\cdot}C_{60}(CH_2Ph)_5$. Multiple addition of dialkoxyphosphoryl radicals to C_{60} proceeds nonregioselectively, and allyl radicals are not formed.[6] The presence of allyl radicals in the reaction mixture has been observed[9] in the stepwise addition of dimethoxyphosphoryl radicals to fullerene C_{70}. The question of why some radicals direct the further addition, and other do not, does not yet have an unequivocal answer.

It was of interest to elucidate whether η^2-metallocomplexes of fullerene (L_2MC_{60}, where M = Pd (**1**) and Pt (**2**), L = PPh_3)[10,11] affect the direction of the addition of phosphoryl radicals.

Experimental

In the experiments, a DRSh-1000 high pressure mercury lamp was used, its filtered or nonfiltered light was used for irradiation of the solutions studied. ESR spectra were recorded on a Varian E-12A spectrometer.

Results and Discussion

A saturated toluene solution of complex **1** was subjected to UV irradiation in the presence of an equimolar amount of $Hg[P(O)(OPr^i)_2]_2$ at 20 °C in the resonator of an ESR spectrometer. Initially, in the ESR spectrum the superposition of signals of at least five radicals with different HFS constants of the unpaired electron with ^{31}P nuclei (55—70 G) and *g*-factors (2.001—2.003) were observed. The parameters of the dominating signal coincided completely with those of the $^{\cdot}C_{60}P(O)(OPr^i)_2$ radical (**3**). After 3—5 min of irradiation, only the spectrum of this radical is observed, and the characteristic green color of a solution of metal-coordinated fullerene disappears. Presumably, the phosphoryl radical attacks complex **1** nonselectively, and the set of signals in the ESR spectrum corresponds to isomeric spin-adducts $L_2Pd^{\cdot}C_{60}P(O)(OPr^i)_2$ (**4**) and demetallated **3** formed as a result of attack on the metal atom. Demetallation reduces all of the isomeric radicals to unsubstituted radical **3**. Previously,[12] phosphoryl Pd and Pt derivatives have been obtained by oxidative addition of mercury salts to Pt(0) and Pd(0) complexes. In addition, we established that compound **1** reacts slowly with $Hg[P(O)(OPr^i)_2]_2$ at *ca.* 20 °C (the degree of conversion is 50 % after 3 days) without irradiation (Scheme 1). Evidently, under UV irradiation (λ = 250—680 nm) the rate of demetallation increases sharply. Thus, η^2-complexes of C_{60} with Pt and Pd are unstable with respect to phosphoryl radicals.

At the initial moment of the reaction, when the concentration of **1** is high and C_{60} is not present in the

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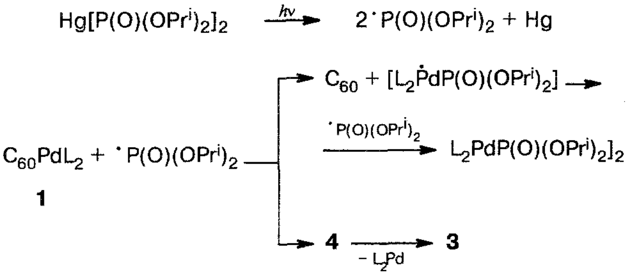
Scheme 1



Scheme 2

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

$$\mathrm{C_{60}} + {}^{\bullet}\mathrm{P(O)(OPr^i)_2} \longrightarrow \underset{\mathbf{3}}{{}^{\bullet}\mathrm{C_{60}P(O)(OPr^i)_2}}$$

$$2\,{}^{\bullet}\mathrm{C_{60}P(O)(OPr^i)_2} \rightarrow \mathrm{(Pr^iO)_2(O)PC_{60}{-}C_{60}P(O)(OPr^i)_2}$$

$$\mathrm{RC_{60}{-}C_{60}R} + 2\,\mathrm{Pt(PPh_3)_4} \rightarrow \underset{\mathbf{5}}{\mathrm{R(PPh_3)_2PtC_{60}{-}C_{60}Pt(PPh_3)_2R}}$$

$$\mathrm{R} = \mathrm{P(O)(OPr^i)_2}$$

$$\underset{\mathbf{5}}{\mathrm{R(PPh_3)_2PtC_{60}{-}C_{60}Pt(PPh_3)_2R}} \xrightarrow{h\nu} \underset{\mathbf{6a{-}e}}{2\,{}^{\bullet}\mathrm{C_{60}Pt(PPh_3)_2R}}$$

solution, phosphoryl radicals add to the fullerene metallocomplex at different distances from the metal atom, which results in the formation of spin-adducts with different *g*-factors and HFS constants. However, the attack of the phosphoryl radical not only on the metal atom, but also on the double bond nearest to the M—C bond can afford a radical in which the M—C bonds are weakened, and elimination of L_2M from the complex gives radical **3**. One also cannot exclude the possibility that in the case of the addition of a phosphoryl radical to a position in C_{60} remote from the metal atom the presence of the metal will not manifest itself in the ESR spectra at all.

In order to obtain supplementary information about the structure of metal-containing spin-adducts we tested Pt complex **2**, containing a magnetic isotope ^{195}Pt (natural abundance 33 %). However, in this case also the pattern observed was similar to that described above, the only difference was that the destruction of the metallocomplex under UV irradiation proceeded even faster (1—2 min), after which only the signal with the parameters of radical **3** was observed in the ESR spectrum. Thus, the interaction of phosphoryl radicals with metallocomplexes of fullerene C_{60} affords unstable spin-adducts, which prevents the investigation of these systems. It is of note that in the absence of $Hg[P(O)(OR)_2]_2$ photodestruction of complexes **1** and **2** in the toluene solution occurs *ca.* 10-fold more slowly. If the main reason for the instability of $^{\bullet}C_{60}ML_2P(O)(OPr^i)_2$ is the weakening of the metal—carbon bonds due to the presence of an unpaired electron in an antibonding orbital, then the same situation should hold in the independent synthesis, *i.e.*, addition of PtL_2 or PdL_2 to the products of the reaction of phosphoryl radicals with C_{60}.

Previously,[6] we have demonstrated that phosphorylfullerenyl radicals undergo reversible dimerization, therefore, we performed the synthesis in two stages. First, the maximum amount of radical **3** dimer was obtained by photolysis of a toluene solution of C_{60} and $Hg[P(O)(OPr^i)_2]_2$ (molar ratio 1 : 0.5), then an equimolar amount of the $Pt(PPh_3)_4$ complex was added to the solution under Ar (analogously to the synthesis of a complex of C_{60} with Pd(0) and Pt(0)).[10,11] The fullerene metallocomplex is formed very rapidly, practically simultaneously with the dissolution of $Pt(PPh_3)_4$ in toluene,

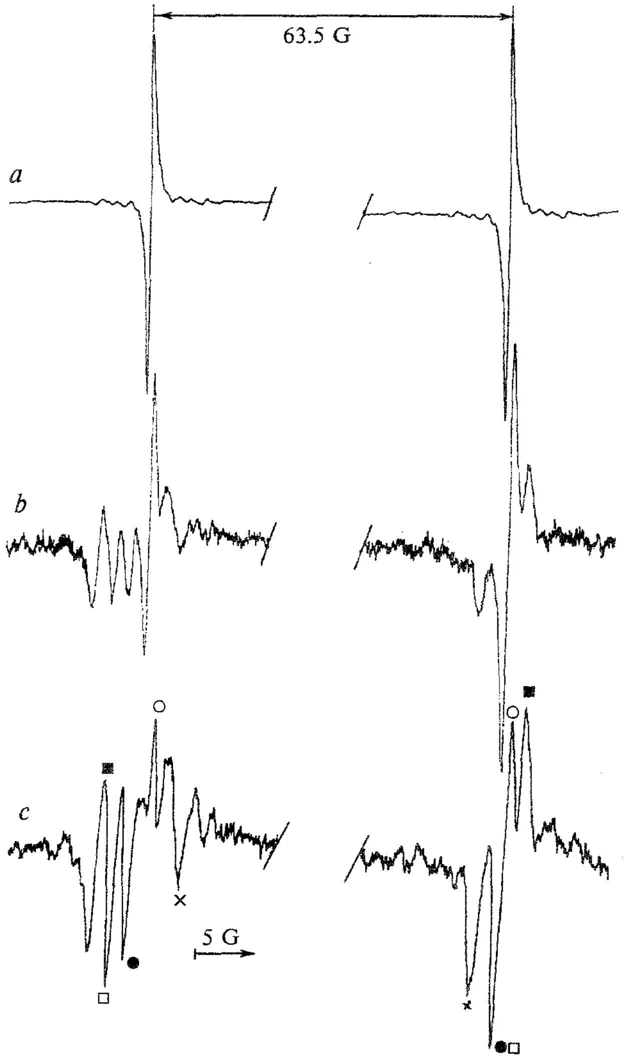


Fig. 1. The ESR spectra at 293 K: *a*, $^{\bullet}C_{60}P(O)(OPr^i)_2$ radical; *b*, isomers of the radical $L_2PtC_{60}^{\bullet}P(O)(OPr^i)_2$ upon addition of PtL_4 to $RC_{60}{-}C_{60}R$ (1 mol. equiv. of PtL_4 per 1 mol. equiv. of C_{60}); *c*, $L_2PtC_{60}^{\bullet}P(O)(OPr^i)_2$ radicals (1.5 mol. equiv. of PtL_4 per 1 mol. equiv. of C_{60}).

and the solution turns dark green. After completion of the reaction, the sample was irradiated with visible light (620—680 nm). In this process new phosphoryl radicals are not generated; only the dimer of fullerenyl radicals, in which C—C bond energy is rather low (*ca.* 10 kcal),[6] is sensitive to this action. Thus, the overall process can be illustrated by Scheme 2.

In fact, as can be seen from Fig. 1, irradiation of the sample with visible light results in the formation of new radicals: **6a** (a_P = 58.5 G, g = 2.0017), **6b** (a_P = 63.5 G, g = 2.0023), **6c** (a_P = 64.7 G, g = 2.0025), **6d** (a_P = 65.7 G, g = 2.0028), and **6e** (a_P = 68.0 G, g = 2.0032). Because of the complex superposition of the ESR signals of radicals **6a—e**, which are approximately equal in intensity, misinterpretation of absorption lines and, consequently, incorrect determination of HFS constants and g-factors are possible. The ESR spectrum of radicals **6a—e** remains unchanged during irradiation (> 60 min) with visible light at 320 K. When the light is switched off, radicals **6a—e** disappear (apparently they undergo dimerization). The results obtained demonstrate that the most probable reason for the instability of adducts of phosphoryl radicals to metallocomplexes is attack of phosphoryl radical on the metal atom.

Thus, we have studied for the first time spin-adducts of metallocomplexes of fullerene C_{60}. It has been shown that the addition of $Pt(PPh_3)_4$ to RC_{60}—$C_{60}R$ proceeds nonselectively. The interaction of the unpaired electron with the metal atom nucleus, located in different positions relative to the radical center, results in variations in the HFS constants and g-factors.

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