Metal-containing fullerenyl radicals: generation in solution and EPR study

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Abstract

Photolysis of *cis*-$(CF_3)_2CF$–Hg–$Pt(PPh_3)_2$–$CH=CPh_2$ in a saturated toluene solution of C_{60} has generated the platinum-centered free radical, which adds to C_{60} to give a spin-adduct *cis*-$Ph_2C=CH$–$Pt(PPh_3)_2$–$C_{60}^{\bullet}$ fully characterized by EPR spectroscopy. Phosphorylfullerenyl radicals containing a η^2-coordinated ML_2 moiety have been prepared, starting from phosphorylfullerenyl radical dimers. The metal complex $(\eta^2$-$C_{70})Pd[(+)DIOP]$ has been shown to undergo the partial rupture of M–C bonding as a consequence of the phosphoryl radical attack on the metal atom to give three regioisomers of metal-containing fullerenyl radicals. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Free-radical chemistry of fullerenes is a substantial part of their reactivity. Fullerenes have been recognized early as free-radical sponges with the capacity to add many radicals [1–3]. EPR spectroscopy proved to be the efficient and most informative tool for investigating the resulting spin-adducts [4–6]. The addition of fullerenes to radicals in which spin density is centered on carbon or various heteroatoms (B, O, P, S etc.) has been studied widely. In mono-adducts $RC_{60}^{\bullet}$, an unpaired electron is delocalized mostly over two neighboring hexagons adjacent to the bond C–CR [7]. These fullerenyl radicals undergo reversible dimerization in solution [8,9].

For organometallic fullerene chemistry, synthesis of the metal-containing fullerenyl radicals and their reactivity are of high interest. Catalytic activity of the stable palladium–fullerene complexes has been demonstrated previously [10] and it is possible to expect catalytic properties of some kind from the metal–fullerenyl radicals. Combination within one molecule of the fullerene core, transition metal, and free-radical center can be done in different ways.

In this paper we wish to describe several routes to the species of this kind: (i) addition to fullerene of a metal-centered radical; (ii) radical attack on the η^2-metal fullerene complex; (iii) introducing the metal into the precursor of a fullerenyl radical, namely, dimer of fullerenyl radical (for preliminary communication, see [11a,b]).

2. Experimental

All the reactions were carried out using the Schlenk technique under an argon atmosphere. Solvents were dried, degassed and distilled under argon.

Synthesis of the mercury–platinum compound used here has been described in our earlier work [12]. Complex $(\eta^2$-$C_{70})Pd[(+)DIOP]$ was prepared similarly to the C_{60} analogue as described previously [13]. EPR spectra have been registered on a Varian E12A spectrometer. Irradiation of the degassed solutions in quartz tubes was made with the focused light of a DRSh-1000 high pressure lamp (1 kW).

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3. Results and discussion

The photosensitive mercury–platinum bond appears to be a good precursor for generating a free radical with an unpaired electron centered on platinum. The general method for preparing compounds of this class was elaborated earlier [12]. Insertion of platinum(0) carbenoid, L_2Pt into the mercury-element bond gives rise to the *cis*-configuration of phosphine ligands L in the planar-square coordinative sphere of platinum. Photolysis of the particular compound **1** with a perfluorinated group at mercury was performed in toluene saturated on C_{60}. The resulting radical **2** adds immediately to fullerene giving the platinumfullerenyl spin-adduct **3**. The EPR spectrum of **3** is shown in Fig. 1 from which the following hyperfine splitting (hfs) constants a can be obtained: a (^{195}Pt) = 52.0, a (P^1) = 3.5, a (P^2) = 30.5 G, g = 2.0013 (Scheme 1).

The large value of $a(^{195}$Pt$)$ is the unambiguous evidence for the direct σ-bonding of platinum to the fullerene core and the localization of spin density on the neighboring carbon atoms. It is worth noting that this species, moderately stable in solution, is still the only representative reported wherein the metal is σ-bonded to fullerene.

Observation of two different hfs constants a_P with two ^{31}P nuclei evidences that these nuclei are non-equivalent. This fact can be explained by the retention of the planar-square arrangement around the platinum atom with two phosphine ligands in the *cis*-position on moving from **1** to **3**. An alternative possibility might be the distortion with the loss of planar geometry around the metal. In this case, phosphorus atoms in **3** may be situated over a pentagon and over a hexagon as shown below.
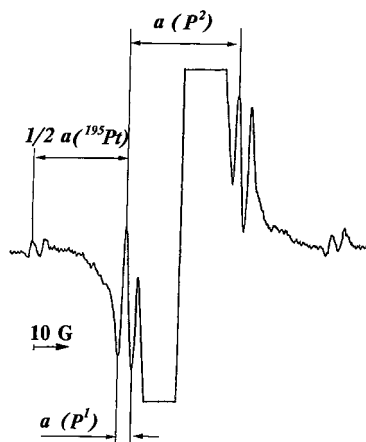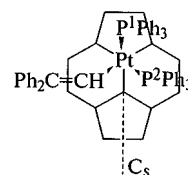

In addition to signals of **3,** a broad line is observed in the center of the EPR spectrum, which is probably due to poly-adducts of C_{60} with carbon-centered fluorinated radicals formed on homolysis of the Hg–R^f bond. It was interesting to investigate the behavior of η^2-metallofullerene complexes under the radical attack, because they have the additional site, the metal itself. We used our favorite phosphoryl radicals [14], easy to prepare and the most informative owing to the characteristic a_P constants. In fact, addition of phosphoryl radicals photolytically generated to $(\eta^2$-$C_{60})M(PPh_3)_2$, where M = Pd or Pt, gives rise to a mixture of several (at least, five) regioisomeric spin-adducts; however, in a few minutes only the characteristic EPR spectrum of pure demetalated parent radical ${}^\bullet C_{60}P(O)(OPr^i)_2$ is left, g = 2.0022, a = 63.5 G [14].

In the search for a more stable fullerene metal complex, we turned to the DIOP complexes reported in our previous work [13,15]. For the C_{60} palladium complex, it was not possible to obtain an EPR spectrum with satisfactory signal/noise ratio, probably due to its low solubility in toluene. Photochemical phosphorylation of $(\eta^2$-$C_{70})Pd(DIOP)$ (**4**) in the EPR tube resulted in the registration of an unusual spectrum (Fig. 2). Besides three doublets asterisked from isomeric spin-adducts of P-radicals with free, demetalated C_{70} (a_P = 70.5 G, g = 2.0031; a_P = 66.5 G, g = 2.0027; a_P = 55.25 G, g = 2.0028), three doublets of doublets were observed with the following parameters: **I(A):** a(P^1) = 30.0 G, a(P^2) = 54.0 G, g = 2.0112; **I(B):** a(P^1) = 30.0 G, a(P^2) = 53.3 G, g = 2.0040; **I(C):** a(P^1) = 30.0 G, a(P^2) = 53.5 G, g = 2.0043.

The patterns resemble the EPR spectrum of species **3** in having two different a_P constants due to non-equivalent phosphorus atoms. The larger a_P may correspond to the phosphoric group while the smaller one to the phosphine P. The latter is the same one as a_P in **3**. The value of the g-factor differs sharply from those of phosphorylfullerenyl radicals. On this basis, we assign the structure **5** to this EPR-active species that can result from the attack by phosphoryl radical on the metal, which causes the conversion of η^2-bonding of palladium in **4** to σ-bonding in palladiumfullerenyl spin-adduct **5** (Scheme 2).

Thus we have shown that the free radicals promote preferential demetalation of η^2-metal–fullerene complexes. However, the indirect route to spin-adducts of
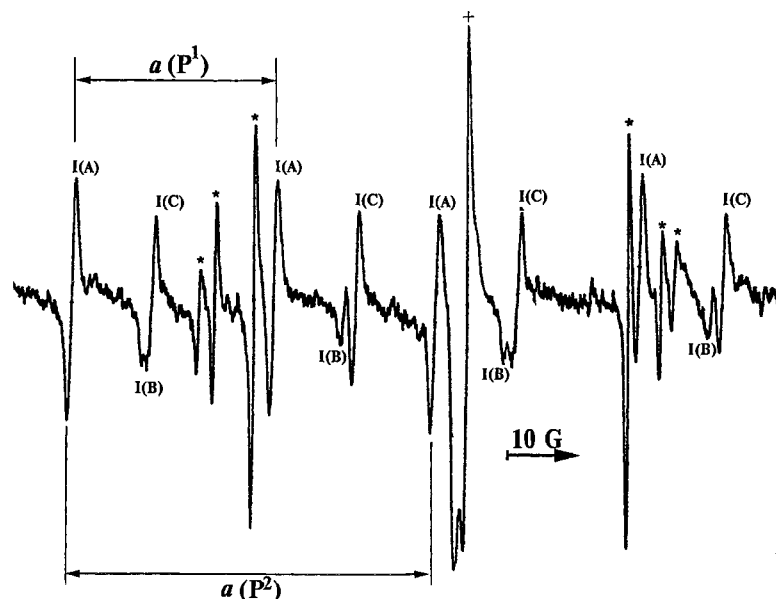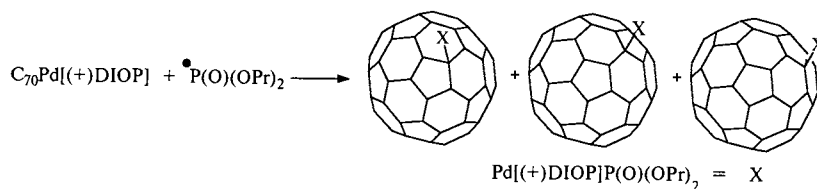

Fig. 1. EPR spectrum of the radical ${}^\bullet C_{60}Pt(PPh_3)_2CH=CPh_2$ at 293 K.
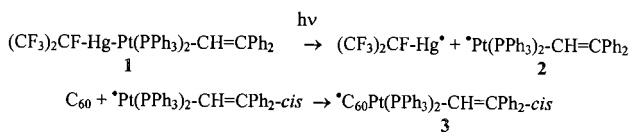
Scheme 1.

Fig. 2. EPR spectra of isomers **I**(A)–**I**(C) of the radical $^\bullet C_{70}Pd(PPh_3)_2P(O)(OPr^i)_2$ at 293 K. (*) $^\bullet C_{70}P(O)(OPr^i)_2$; (+) signal of quartz tube.
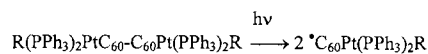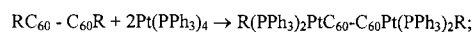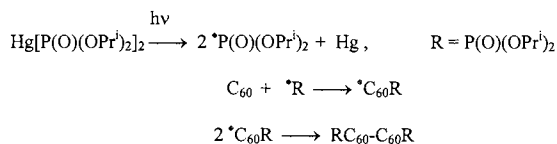

Scheme 2.

these η^2-metal complexes is possible using the reactivity of fullerene dimers and their ability to dissociate under irradiation with visible light. The reaction sequence is shown in Scheme 3.

First, the maximum amount of dimer $RC_{60}-C_{60}R$ was obtained by photolysis of the 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. The fullerene metallocomplex is formed very rapidly, practically simultaneously with the dissolution of $Pt(PPh_3)_4$ in toluene, and the solution turns dark green. After completion of the reaction, the sample was irradiated with visible light (620–680 nm). In fullerenyl radical dimers, the C–C bond energy is rather low (ca. 10 kcal), less than that of the P–Hg bond. So, in this process, new phosphoryl radicals are not generated, only the dissociation of the dimer of platinated phosphorylfullerenyl radicals occurs. A similar result was obtained when the dimer was η^2-platinated using the retro-insertion reaction [11b].

In fact, as can be seen from Fig. 3, irradiation of the sample with visible light results in the formation of new radicals: **II**(A) ($a_P = 58.5$ G, $g = 2.0017$), **II**(B) ($a_P = 63.5$ G, $g = 2.0023$), **II**(C) ($a_P = 64.7$, G, $g = 2.0025$) **II**(D) ($a_P = 65.7$ G, $g = 2.0028$), **II**(E) ($a_P = 68.0$ G, $g = 2.0032$). Because of the complex superposition of

the EPR signals of radicals **II**(A–E), which are approximately equal in intensity, misinterpretation of absorption lines and, consequently, incorrect determination of hfs constants and g-factors are possible. The EPR spectrum of radicals **II**(A–E) remains unchanged during irradiation (> 60 min) with visible light at 320 K. When the light is switched off, radicals **II**(A–E) disappear (apparently they undergo dimerization). Thus, 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. To our knowledge, this is the first synthetic application of dimers of the fullerenyl radicals.
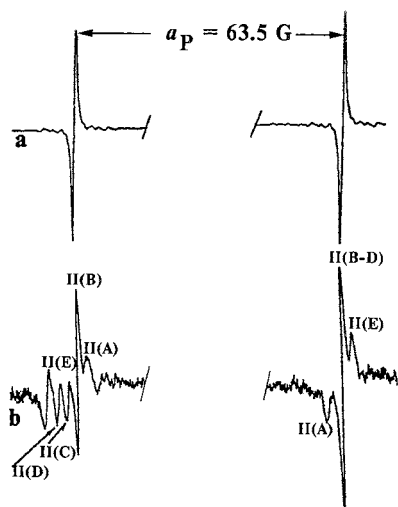
$$Hg[P(O)(OPr^i)_2]_2 \xrightarrow{h\nu} 2\,^\bullet P(O)(OPr^i)_2 + Hg\,, \qquad R = P(O)(OPr^i)_2$$

$$C_{60} + \,^\bullet R \longrightarrow \,^\bullet C_{60}R$$

$$2\,^\bullet C_{60}R \longrightarrow RC_{60}\text{-}C_{60}R$$

$$RC_{60}\text{-}C_{60}R + 2Pt(PPh_3)_4 \rightarrow R(PPh_3)_2PtC_{60}\text{-}C_{60}Pt(PPh_3)_2R;$$

$$R(PPh_3)_2PtC_{60}\text{-}C_{60}Pt(PPh_3)_2R \xrightarrow{h\nu} 2\,^\bullet C_{60}Pt(PPh_3)_2R$$

Scheme 3.

Fig. 3. EPR spectra at 293 K; (a) $^{\bullet}C_{60}P(O)(OPr^i)_2$ radical; (b) isomers of the radical $(PPh_3)_2PtC_{60}^{\bullet}P(O)(OPr^i)_2$ formed after addition of $Pt(PPh_3)_4$ to RC_{60}–$C_{60}R$ (1 molar equivalent $Pt(PPh_3)_4$ per 1 molar equivalent of C_{60}) and irradiation with visible light.

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