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Note

Photoreactivity of buckminsterfullerenebis(triphenylphosphite)platinum(0) induced by metal-to-ligand charge transfer excitation

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Abstract

The complex $C_{60}Pt[P(OPh)_3]_2$ displays $C_{60} \pi \pi^*$ intraligand bands in the UV-Vis region and a long-wavelength absorption at $\lambda_{max} = 770$ nm which is assigned to a metal-to-ligand charge transfer (MLCT) transition from platinum to fullerene. The irradiation of the complex leads to the population of the reactive MLCT state and subsequently to the dissociation $(C_{60}Pt[P(OPh)_3]_2 \rightarrow C_{60} + Pt[P(OPh)_3]_2)$ in the primary photochemical step. Product formation takes place by the interception of $Pt[P(OPh)_3]_2$ with suitable scavengers such as CHCl₃ or O_2 .

Keywords: Charge transfer; Platinum(0) complexes; Fullerene complexes

1. Introduction

Although excited state properties of fullerenes have been investigated extensively [1-16] little attention has been paid to fullerene transition metal complexes [17]. Such studies should not only be interesting in their own right but might also provide important contributions to the general field of fullerene research [18,19]. We explored this possibility and selected the complex C60Pt[P(OPh)3]2 for the present investigation. This compound is particularly suited for an initial study since it is rather stable and well characterized [20]. The examination of its excited state behavior is facilitated by previous calculations on the electronic structure of $C_{60}Pt(PH_3)_2$ [21,22] which serves as a model compound for related phosphine and phosphite complexes. It is expected that charge transfer interaction between C_{60} and the Pt(PR₃)₂ fragment determines the excited state behavior of the title complex. Owing to the d¹⁰ electron configuration of Pt(0) any interference by ligand field excited states is thus excluded.

2. Experimental

2.1. Materials

The complex $C_{60}Pt[P(OPh)_3]_2$ was prepared according to a published procedure [20]. The solvents chloroform and toluene were spectrograde.

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2.2. Photolyses

The light source was an Osram HBO 200 W/2 or an Osram XBO 450 W/4 lamp. In all cases the light beam was focused on a thermostated photolysis cell by a quartz lens. The cutoff filter Schott WG 345/3 (λ_{irr} > 320 nm) was used to avoid short-wavelength irradiation. For quantum yield determinations monochromatic light around 770 nm was obtained by a Schoeffel GM 250/1 high-intensity monochromator.

The photolyses were carried out in solutions of CHCl₃ or toluene saturated by air or argon. Progress of the photolyses was monitored by UV–Vis spectrophotometry. C_{60} as a photoproduct was identified by its absorption [12] and fluorescence [10] spectrum.

For the detection of the emission the photolyzed solution was first evaporated. The starting complex and the photolysis products except C_{60} were then removed by extraction with THF. The residual C_{60} was redissolved in toluene and identified by luminescence spectroscopy. For comparison a dark sample was treated by the same procedure. For quantum yield determinations the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. Absorbed light intensities were determined by a Polytec pyroelectric radiometer which was calibrated and equipped with an RkP-345 detector.

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2.3. Instrumentation

Absorption spectra were measured with a Hewlett Packard 8452A diode array or a Shimadzu UV-2100 absorption spectrometer. Emission and excitation spectra were obtained on an Hitachi 850 spectrofluorimeter equipped with a red-sensitive Harnamatsu 928 photomultiplier.

3. Results

The complex C₆₀Pt[P(OPh)₃]₂ was almost insoluble in ethanol and acetonitrile but slightly soluble in chloroform, THF and toluene. These solutions were green in distinction to those of C_{60} which were purple. The absorption spectrum of the complex was somewhat dependent on the solvent (Table 1; Figs. 1 and 2). C₆₀Pt[P(OPh)₃]₂ did not show any emission up to 900 nm in solution at r.t. or in toluene glasses at 77 K. The photochemistry of the complex was studied in CHCl₃ and toluene. The photolyses were restricted to irradiations above 320 nm in order to avoid light absorption by the solvents. Under these conditions free C60 was essentially light stable. Upon irradiation of C60Pt[P(OPh)3]2 in CHCl₃ spectral changes were observed (Fig. 1) which indicated the formation of free C_{60} ($\lambda_{max} = 328, 380, 392, 407,$ 410, 423 and 430 nm). The release of C_{60} was also confirmed by the detection of its fluorescence [10]. The isosbestic points at 324 and 332 nm were preserved for extended irradiation times. The photolysis took place in the presence or absence of oxygen. In deaerated solutions of toluene the complex was almost not light sensitive while upon exposure to oxygen C₆₀Pt[P(OPh)₃]₂ underwent a photolysis with spec-

Table 1

Absorption maxima of C60Pt[P(OPh)3]2 in various solvents

Solvent Chloroform	λ_{\max} (nm) (ϵ (cm ⁻¹ mol ⁻¹ l))				
	330 (37300)	434 (8200)	591 (3100)	640 (2400)	764 (430)
THF	336	434	596	638	765
	(29000)	(7300)	(2870)	(2300)	(400)
Toluene	339	434	588	634	776
	(40300)	(9700)	(3700)	(2700)	(400)



Fig. 1. Spectral changes during the photolysis of 4.78×10^{-5} m C_{60} Pt[P(OPh)₃]₂ in CHCl₃ at 0 (a), 5, 15 and 25 min (d) irradiation time, $\lambda_{irr} > 320$ nm; 1 cm cell.



Fig. 2. Spectral changes during the photolysis of 5.97×10^{-5} m $C_{so}Pt[P(OPh)_3]_2$ in toluene at 0 (a), 15, 30 and 60 min (d) irradiation time, $\lambda_{trr} > 320$ nm; 1 cm cell.

tral variations (Fig. 2) which were similar to those in CHCl₃. The spectral changes which accompanied the photolysis in toluene were again in agreement with the formation of free C₆₀. It was also identified by its fluorescence spectrum. The isosbestic points at 319, 347, 385, 423, 460 and 536 nm remained sharp up to 60 min irradiation time. Deviations at later stages of the photolysis indicated a secondary photolysis. Since free C₆₀ does not absorb above 700 nm, the longestwavelength maximum of the complex near 770 nm was used to monitor the complex concentration during the photolysis. The quantum yield for the disappearance of C₆₀Pt-[P(OPh)₃]₂ was $\phi = 2.5 \times 10^{-4}$ in CHCl₃ ($\lambda_{irr} = 764$ nm) and $\phi = 8 \times 10^{-4}$ in air-saturated toluene at $\lambda_{irr} = 776$ nm.

4. Discussion

Free C₆₀ is not a strong electron do. r but a powerful acceptor [17–19]. On the contrary, the electron-rich Pt[P(OPh)₃]₂ fragment is characterized by its electron donating ability. In agreement with these properties, calculations on the model complex C₆₀Pt(PH₃)₂ revealed that the LUMO is largely localized at the C₆₀ ligand while the HOMO originates from the Pt(PH₃)₂ moiety [21,22]. Since the interaction of platinum with the fullerene is essentially restricted to two adjacent carbon atoms of C₆₀ the bonding pattern is similar to that of (C₂H₄)Pt(PH₃)₂ [21,22].

Below 700 nm the absorption spectrum of C₆₀Pt[P(OPh)₃]₂ (Table 1; Figs. 1 and 2) is dominated by $\pi\pi^*$ intraligand (IL) absorptions of C₆₀ which are slightly shifted in comparison to the free fullerene. Deviations might be caused by the perturbation of the electronic structure of C₆₀ upon coordination or by the presence of additional absorption bands in the spectrum of the complex. However, while free C60 does not absorb above 700 nm, $C_{60}Pt[P(OPh)_3]_2$ shows a conspicuous absorption with a maximum around 770 nm (Table 1) which does not seem to belong to the isolated Pt[P(OPh)₃]₂ moiety. Pt(PPh₃)₂ and most likely also analogous phosphite complexes are colorless and do not display absorptions above 400 nm [23]. In agreement with the calculations on $C_{60}Pt(PH_3)_2$ [21,22] and in analogy to $(C_2H_4)Pt(PH_3)_2$ [24] we assign the longestwavelength absorption of C60Pt[P(OPh)3]2 at 770 nm to a metal-to-ligand charge transfer (MLCT) transition involving the promotion of an electron from the d¹⁰ metal center to a π^* orbital of the fullerene ligand.

While free C_{60} shows a fluorescence [10] the fullerene ligand of C_{60} Pt[P(OPh)₃]₂ is not luminescent. It is assumed that the $\pi\pi^*$ IL states of C_{60} are deactivated to the MLCT state at lower energies. Finally, the MLCT state is reactive and initiates a dissociation in analogy to (C_2H_4) Pt(PH₃)₂ [24]. The photoreactivity is certainly based on the C_{60} -Pt antibonding nature of the π^* orbital which is populated in the MLCT excited state.

In the primary photochemical step the fullerene is apparently released:

$$C_{60}$$
Pt[P(OPh)₃]₂ \rightarrow C_{60} +Pt[P(OPh)₃]₂

In the absence of any scavenger the starting complex is regenerated. However, in the presence of suitable species the reactive fragment $Pt[P(OPh)_3]_2$ is intercepted and stable photoproducts are formed.

Chlorinated alkanes such as CHCl₃ can add oxidatively to reactive metal centers in various ways. According to previous observations on the photooxidation of platinum compounds by CHCl₃ or CH₂Cl₂ [24–26], several complexes such as PtHCl[P(OPh)₃]₂, PtCl(CHCl₂)[P(OPh)₃]₂ and PtCl₂[P(OPh)₃]₂ may have been generated during the photopsis of C₆₀Pt[P(OPh)₃]₂. Unfortunately an analysis of the photoproducts which were formed in addition to C₆₀ was hampered by the small efficiency of the photolysis and the low solubility of the starting complex. However, the essential conclusions of the present study do not depend on the results of such an analysis.

In toluene solutions $Pt[P(OPh)_3]_2$ can be scavenged by oxygen. It is assumed that $PtO_2[P(OPh)_3]_2$ was formed in agreement with the general behavior of $Pt(PR_3)_n$ complexes towards oxygen [27]. The secondary photolysis which was observed upon irradiation of $C_{60}Pt[P(OPh)_3]_2$ in air-saturated toluene at longer irradiation times may be related to the light sensitivity of the dioxygen complex. $PtO_2(PPh_3)_2$ was reported to undergo a photodissociation into $Pt(PPh_3)_2$ and singlet oxygen [28].

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