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Preliminary communication

Photo-oxidation of bis[1,2-bis(diphenylphosphino)ferrocene]-palladium(0) in CCl_4 induced by ferrocene to solvent charge transfer excitation

Horst Kunkely, Arnd Vogler *

Institut für Anorganische Chemie, Universität Regensburg, D-93040 Regensburg, Germany

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Abstract

The electronic spectrum of $Pd^0[(PPh_2C_5H_4)_2Fe^{II}]_2$ in CCl_4 shows an absorption at $\lambda_{max} = 338$ nm that is assigned to a charge transfer-to-solvent (CTTS) transition from the ferrocene moiety to CCl_4. The CTTS excitation leads to the formation of $Pd^{II}[(PPh_2C_5H_4)_2Fe^{II}]Cl_2$. It is suggested that the irradiation induces initially the generation of Fe^{III}, which then oxidizes Pd^0 by intramolecular electron transfer. Product formation takes place by a disproportionation of Pd^I. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Charge transfer; Palladium complexes; Ferrocene complexes; Photochemistry

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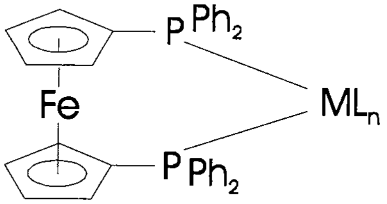
1. Introduction

Polynuclear heterometallic transition metal complexes have attracted much attention in recent years. This interest is related to the importance of these compounds in various fields, such as biochemistry and catalysis. These functions depend on several effects, including electronic coupling of the metal centers. Under suitable conditions, the metal–metal interaction generates an electronic metal-to-metal charge transfer (MMCT) transition that appears as an absorption in the electronic spectrum [1–6]. MMCT excitation can result in a photoredox reaction [4,5]. As another intriguing possibility, a photoredox process may take place at one metal center but subsequent electron transfer creates a change of the redox state at the second metal. This type of process might be important for applications in supramolecular photochemistry [7,8], e.g. molecular electronics and artificial photosynthesis. A suitable polynuclear complex that could serve as a simple model is represented by the structure [9]:



In chlorinated solvents, ferrocene shows a photoactive charge transfer-to-solvent (CTTS) absorption [10,11]. CTTS excitation leads to the oxidation of Fe^{II} to Fe^{III}. If the second metal M is reducing, the photooxidation may be followed by an electron transfer from M to Fe^{III}. As a result, the ferrocene moiety would finally remain chemically intact, while only the second metal is oxidized. We explored this possibility and selected the complex $Pd^0[(PPh_2C_5H_4)_2Fe^{II}]_2$ [12] with $Fe^{II}(C_5H_4PPh_2)_2$ denoting 1,1′-bis(diphenylphos-

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* Corresponding author. Tel.: +49 941 9434485; fax: +49 941 9434488.

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phine)ferrocene (BDPF) for the present study. This choice was based on several previous observations. Our target complex is easy to synthesize and should undergo a facile oxidation to Pd(II). Moreover, our recent study of $\{Re^{I}[(PPh_2C_5H_4)_2Fe^{III}](CO)_3Cl\}^+$ has shown that Fe and Re are sufficiently coupled to provide an efficient path for electron transfer [13]. Accordingly, $Pd^0(BDPF)_2$ should be an excellent candidate for ferrocene to R–Cl CTTS-induced photo-oxidation of Pd^0.

2. Results

The electronic spectrum of $Pd^0(BDPF)_2$ in CH_3CN (Fig. 1) shows an absorption maximum at $\lambda = 450$ nm ($\varepsilon = 1200$ M^{-1} cm^{-1}) and a shoulder at $\lambda = 270$ nm (24000). In CCl_4, which has a solvent cut-off at $\lambda < 270$ nm, the long-wavelength band now appears as a shoulder at 462 nm ($\varepsilon = 1500$), while a rather intense new band shows up (Fig. 1) at $\lambda_{max} = 338$ nm (9100).

Upon irradiation (Hanovia Xe/Hg 977 B-1 lamp) of $Pd^0(BDPF)_2$ in CCl_4 with $\lambda_{irr} > 300$ nm, a photolysis takes place that does not depend on the presence of oxygen. This photoreaction is associated with spectral changes (Fig. 2) that result in a general growth of the absorbance over the entire UV–vis spectral region. This apparent absorption, which increases towards shorter wavelengths, is caused by light scattering at colloidal particles. The colloidal photoproduct is separated by centrifugation, and identified as $Pd(BDPF)Cl_2$ by its UV spectrum in CCl_4 ($\lambda_{max} = 336$ nm, $\varepsilon = 7200$ and 276 nm, $\varepsilon = 41600$) and IR spectrum of a solid sample ($\bar{\nu}$ Pd–Cl: 260 and 248 cm^{-1}) [12]. Since the absorption spectra of $Pd(BDPF)_2$ and $Pd(BDPF)Cl_2$ are dominated by the bands of the BDPF ligand, they are quite similar. Accordingly, the spectral variations during the photolysis of $Pd(BDPF)_2$ are not accompanied by the appearance of new absorption features (Fig. 2). However, $Pd(BDPF)Cl_2$ is less soluble than $Pd(BDPF)_2$, and separates as a colloid from the homogenous solution. The stoichiometry of this photoreaction is established by the following procedure. The colloid of a partially photolyzed solution is separated by centrifugation and redissolved in CCl_4. This solution, as well as the clear solution obtained from centrifuging, were spectrophotometrically analyzed for $Pd(BDPF)Cl_2$ and $Pd(BDPF)_2$, respectively. This determination yields a ratio of 1:0.78 for $Pd(BDPF)_2$ to $Pd(BDPF)Cl_2$. The progress of the photolysis is monitored by measuring the increase of the optical density at 700 nm. The determination of the relative quantum yields for the formation of $Pd(BDPF)Cl_2$ is based on this increase of the apparent absorption at this wavelength. Monochromatic light was obtained using a Schoeffel GM 250/1 high-intensity monochromator. The absorbed light intensities were determined by a Polytec pyroelectric radiometer, which was calibrated by actinometry and equipped with a RkP-345 detector. The quantum yields are strongly dependent on the irradiating wavelength. While they reach a maximum at $\lambda_{irr} = 333$ nm ($\phi_{rel} = 1.0$), they are relatively small at $\lambda_{irr} = 313$ nm ($\phi_{rel} = 0.5$), 366 nm (0.17) and 405 nm (0.07).

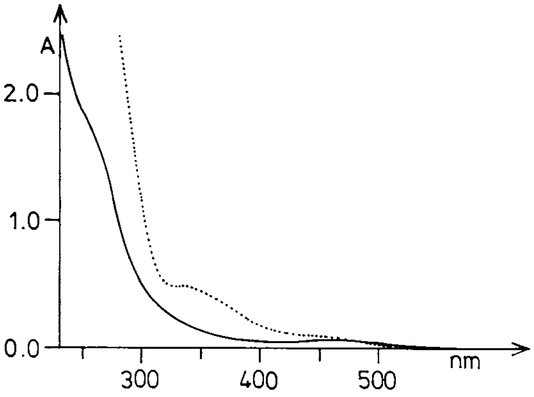

Fig. 1. Electronic absorption spectra of 5.47×10^{-5} M $Pd(BDPF)_2$ in CH_3CN (—) and CCl_4 (......) at r.t., 1 cm cell.

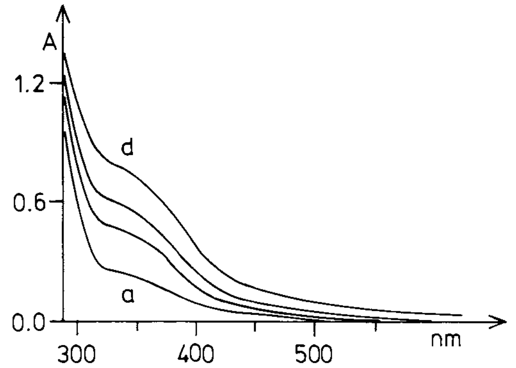

Fig. 2. Spectral changes during the photolysis of 2.74×10^{-5} M $Pd(BDPF)_2$ in CCl_4 at r.t. after 0 (a), 2 (b), 4 (c) and 8 (d) min irradiation time with $\lambda_{irr} = 333$ nm, 1 cm cell.

3. Discussion

The electronic spectrum of $Pd(BDPF)_2$ in CH_3CN (Fig. 1) shows long-wavelength absorptions that belong only to the BDPF ligand. This conclusion is consistent with the observation that $Pd^0(PPh_3)_4$ displays its longest-wavelength band at $\lambda_{max} = 322$ nm [14]. The longest-wavelength absorption of $Pd(BDPF)_2$ at $\lambda_{max} = 450$ nm is assigned to the lowest-energy ligand field (LF) transition of the ferrocene moiety [6,10,11]. Ferrocene ($\lambda_{max} = 440$ nm) and many of its derivatives, show this characteristic absorption band in the same wavelength region. If $Pd(BDPF)_2$ is dissolved in CCl_4, a new intense absorption appears at $\lambda_{max} = 338$ nm. In analogy to ferrocene [10,11], this band is assigned to a CTTS transition from the ferrocene moiety to the halocarbon solvent.

CTTS excitation of ferrocene in chlorinated alkanes leads to the oxidation of ferrocene to the ferrocenium cation [10,11]:

$$\mathrm{Fe^{II}Cp_2 + R \ngtr Cl \xrightarrow{h\nu} [Fe^{III}Cp_2]^+ Cl^- + R^{\bullet}}$$

There is little doubt that the same type of CTTS excitation of $Pd(BDPF)_2$ also induces the photo-oxidation of a ferrocene moiety:

$$\mathrm{\{Pd^0[(PPh_2C_5H_4)_2Fe^{II}]_2\}}$$
$$\mathrm{+ CCl_4 \xrightarrow{h\nu} \{Pd_0[(PPh_2C_5H_4)_2Fe^{III}][(PPh_2C_5H_4)_2Fe^{II}]\}^+}$$
$$\mathrm{+ Cl^- + {}^{\bullet}CCl_3}$$

However, the ferrocenium cation is not present in the final photoproduct, as indicated by the absence of a diagnostic absorption band at 620 nm [6,10,11,15]. Ferrocenium is a strong oxidant and is apparently able to oxidize Pd^0:

$$\mathrm{\{Pd^0[(PPh_2C_5H_4)_2Fe^{III}][(PPh_2C_5H_4)_2Fe^{II}]\}^+}$$
$$\mathrm{\rightarrow \{Pd^I[(PPh_2C_5H_4)_2Fe^{II}]_2\}^+ Cl^-}$$

Product formation can now occur by a subsequent disproportionation of Pd^I:

$$\mathrm{2[Pd^I(BDPF)_2]^+ Cl^-}$$
$$\mathrm{\rightarrow Pd^0(BDPF)_2 + Pd^{II}(BDPF)Cl_2 + BDPF}$$

In summary, the outer sphere photo-oxidation of the ferrocene moiety of $Pd^0(BDPF)_2$ is followed by a facile intramolecular electron transfer from Pd^0 to Fe^{III}, which finally leads to Pd^{II} as a stable photoproduct. This novel photoredox process represents a special type of photo-induced electron transfer in polynuclear complexes and may be important for applications in supramolecular photochemistry.

Acknowledgements

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