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Journal of Organometallic Chemistry 559 (1998) 223–225

Journal of Organometallic Chemistry

Preliminary communication

# Electronic spectrum and photoreactivity of dichloro(1,5-cyclooctadiene)-palladium(II)

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Received 8 January 1998

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## Abstract

The complex $Pd^{II}(1,5\text{-COD})Cl_2$ (1,5-COD = 1,5-cyclooctadiene) shows a long-wavelength ligand-to-metal charge transfer (LMCT) absorption at $\lambda_{max} = 342$ nm. It is suggested that LMCT excitation generates a COD radical cation and $Pd^{I}Cl_2^-$ in the primary photochemical step. In acetonitrile, a back-electron transfer takes place that leads to the transformation of 1,5-COD to its 1,3-isomer and a solvated Pd(II) complex. In ethanol, the COD radical cation and $Pd^I$ are reduced by the solvent, which is oxidized to acetaldehyde. Metallic palladium is formed as a colloid.

*Keywords:* Absorption spectra; Palladium complexes; Photochemistry

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## 1. Introduction

Olefin complexes play an important role in organometallic chemistry. A variety of such complexes is light sensitive [1]. Photo-induced substitutions, isomerizations and oxidative additions of olefin ligands have been observed. Generally, these photoreactions can be related to electronic transitions that require the participation of the olefin. Frequently, the reactive excited states are of the metal → $\pi^*$ (olefin) metal-to-ligand charge transfer (MLCT) and $\pi\pi^*$ (olefin) intraligand (IL) type. In this context, it is quite surprising that olefin → metal ligand-to-metal charge transfer (LMCT) transitions that could initiate olefin oxidation and metal reduction have been largely ignored, although olefins are well-known to be thermally oxidized by many metal complexes [2]. Partly, this lack of interest is related to the fact that the co-ordination of olefins requires metals in low oxidation states that are usually reducing and not oxidizing. In order to fill this gap we searched for suitable complexes and decided to study the compound $Pd^{II}(1,5\text{-COD})Cl_2$ (1,5-COD = 1,5-cyclooctadiene).

Palladium(II) is only weakly reducing, but also oxidizing. It can be easily reduced to metallic palladium. In fact, the ethylene oxidation to acetaldehyde by $Pd^{2+}$ in aqueous solution forms the basis of the Wacker process [3]. However, the mechanism of this olefin oxidation is rather complicated and does not simply involve electron transfer from ethylene to Pd(II). Nevertheless, palladium(II) olefin complexes are promising candidates for photoredox reactions initiated by LMCT excitation. Mono-olefin complexes are quite unstable and reactive and thus, less suitable for our purpose. On the contrary, $Pd(1,5\text{-COD})Cl_2$ is rather stable and easily accessible [4–6].

## 2. Results

The electronic spectrum of $Pd(1,5\text{-COD})Cl_2$ in $CH_3CN$ (Fig. 1) shows absorptions at $\lambda_{max} = 400$ ($\varepsilon =$

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*PII* S0022-328X(98)00483-5

660 dm$^3$ M$^{-1}$ cm$^{-1}$), 342 (1930), 298 (3200), 273 (4650), 240 (sh, 7200) and 219 nm (16200). In solution of ethanol, the maxima are blurred. The complex does not emit at r.t. or at 77 K, but solutions are light sensitive.

The photolysis of Pd(1,5-COD)$Cl_2$ in ethanol is accompanied by spectral variations (Fig. 2) that show an increase of the optical density over the entire visible absorption spectrum. This increase is associated with a brown coloration, which indicates the formation of colloidal palladium [7]. Moreover, the irradiation leads to the evolution of a new band that appears as a shoulder at around 240 nm (Fig. 2). This absorption is attributed to 1,3-cyclooctadiene ($\lambda_{max} = 238$ nm, $\varepsilon = 5900$). Protons and acetaldehyde, which is identified as an addition product of 4-hydroxydiphenyl ($\lambda_{max} = 560$ nm) [8], are further photoproducts. The light-sensitivity of Pd(1,5-COD)$Cl_2$ extends over the whole absorption spectrum, including the 342 nm band.

If the photolysis is carried out in acetonitrile, only traces of elemental palladium are formed. At a longer wavelength ( > 280 nm), all absorptions of Pd(1,5-COD)$Cl_2$ decrease in intensity, but at shorter wavelengths, the appearance of the 240 nm band is again indicative of the formation of 1,3-cyclooctadiene (Fig. 3). The photoreaction is not influenced by oxygen and also proceeds under argon. The photolysis is monitored by measuring the decrease of the optical density at 342 nm. The quantum yields for the disappearance of Pd(1,5-COD)$Cl_2$ are $\phi = 0.08$ at $\lambda_{irr} = 366$ nm and $\phi = 0.03$ at $\lambda_{max} = 405$ nm.

## 3. Discussion

The electronic spectrum of Pd(1,5-COD)$Cl_2$ (Fig. 1) shows a rather complicated pattern, but the two longest-wavelength bands at 400 and 342 nm can be assigned with some confidence. It is suggested that the band at 400 nm ($\varepsilon = 660$) belongs to the lowest-energy spin-allowed LF (ligand field) transition, which appears for several other Pd(II) complexes [9] including Pd(en)$Cl_2$ ($\lambda_{max} = 374$ nm, $\varepsilon = 292$) [10] in the same wavelength region. The higher intensity of the 400 nm band of Pd(1,5-COD)$Cl_2$ is certainly caused by the strong overlap with the 342 nm absorption. This latter band is too intense ($\varepsilon = 1930$) for a LF transition. An IL (COD) transitions can be also ruled out since free 1,5-COD only absorbs at a very short wavelength ($\lambda_{max} = 198$ nm). As the next possibility, a MLCT assignment must be considered. Various other 1,5-COD complexes of metals in low oxidation states display low-energy M → π* (COD) MLCT bands [11–13]. For example, Pt(1,5-COD)$Cl_2$ shows this absorption at $\lambda_{max} = 256$ nm [14]. However, a comparison of Pt(bipy)$Cl_2$ and Pd(bipy)$Cl_2$ has shown that the MLCT (M → bipy) band of the palladium complex ($\lambda_{max} = 318$ nm, in water) occurs at shorter wavelength than that of the platinum compound ($\lambda_{max} = 340$ nm, in water) in agreement with the expectation [15]. Accordingly, a MLCT band of Pd(1,5-COD)$Cl_2$ should appear below 256 nm.

As the only remaining alternative, we assign the 342 nm band of Pd(1,5-COD)$Cl_2$ to a LMCT transition from π-bonding orbitals of COD to Pd(II). Since

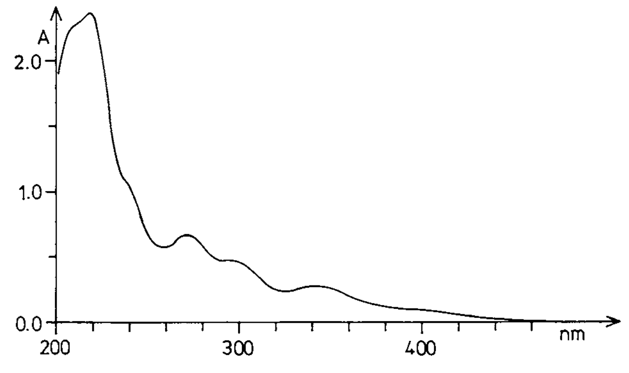

Fig. 1. Electronic absorption spectrum of $1.46 \times 10^{-4}$ M Pd$^{II}$(1,5-COD)$Cl_2$ at r.t. in acetonitrile; 1 cm cell.

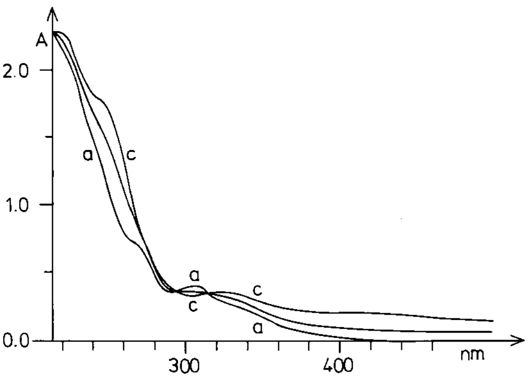

Fig. 2. Spectral changes during the photolysis of $2.07 \times 10^{-4}$ M Pd$^{II}$(1,5-COD)$Cl_2$ in EtOH at r.t. after 0 (a), 4 (b) and 16 (c) min irradiation time with white light (Osram HBO 100 W/2); 1 cm cell.

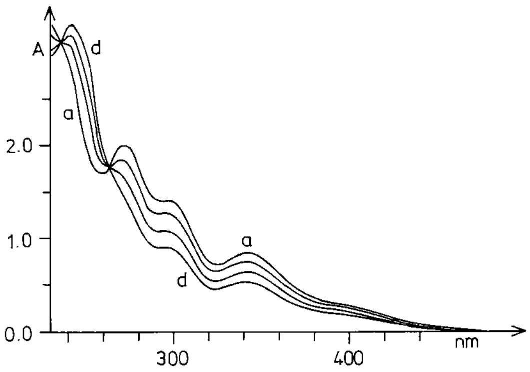

Fig. 3. Spectral changes during the photolysis of $4.36 \times 10^{-4}$ M Pd$^{II}$(1,5-COD)$Cl_2$ in $CH_3CN$ at r.t. after 0 (a), 20 (b), 40 (c) and 100 (d) s irradiation time with white light; 1 cm cell.

olefins are generally reducing, and Pd(II) is oxidizing, such LMCT absorptions should occur at relatively long wavelength in analogy to other Pd(II) complexes with reducing ligands [9]. For example, the lowest-energy LMCT band of $[Pd(N_3)_4]^{2-}$ appears at $\lambda_{max} = 324$ nm ($\varepsilon = 17700$) [7]. Finally, the LMCT assignment of the 342 nm band of Pd(1,5-COD)$Cl_2$ is also consistent with the photochemical properties of this complex.

It is assumed that the photolysis of Pd(1,5-COD)$Cl_2$ is initiated by COD-Pd(II) LMCT excitation. In the primary photochemical step a radical pair should be formed:

$$Pd^{II}(1{,}5-COD)Cl_2 \xrightarrow{h\nu} COD^{\cdot +}\ Pd^{I}Cl_2^{-}$$

It may undergo recombination or cage escape. In acetonitrile, solution back-electron transfer leads to product formation. The reduction of the COD radical cation is apparently associated with the formation of the 1,3-COD isomer. In this context it is quite interesting that the photochemical rearrangement of 1,5-COD to 1,3-COD is also catalyzed by Rh(I), although the mechanism of this reaction is not quite clear [1,16]. Finally, the reoxidation of the $Pd^{I}Cl_2^{-}$ fragment to Pd(II) leads probably to the attachment of acetonitrile as ligands. Since *cis*- or *trans*- $Pd(CH_3CN)_2Cl_2$ as possible photoproducts are not expected to absorb strongly, the spectral variations during the photolysis of Pd(1,5-COD)$Cl_2$ in $CH_3CN$ are not accompanied by the appearance of new long-wavelength bands (Fig. 3). The overall reaction is assumed to proceed according to the equation:

$$Pd^{II}(1{,}5-COD)Cl_2 \xrightarrow{h\nu/CH_3CN} Pd^{II}(CH_3CN)_2Cl_2 + 1{,}3 - COD$$

At this point it should be mentioned that photosubstitutions initiated by LMCT excitation are quite common reactions in inorganic photochemistry. In particular, Co(III) ammine complexes show this type of LMCT reactivity [17].

In ethanol the photolysis of Pd(1,5-COD)$Cl_2$ takes a different course. The solvent is apparently able to reduce the primary radical pair $COD^{\cdot +}\ Pd^{I}Cl_2^{-}$. Product formation takes place according to the equation:

$$Pd^{II}(1{,}5-COD)Cl_2 + C_2H_5OH \xrightarrow{h\nu} Pd^0 + 1{,}3-COD + 2HCl + CH_3CHO$$

In summary, it should be emphasized that although the observation of a reactive LMCT state involving an olefin ligand is rather new, it is not surprising in view of the reducing properties of olefins.

## Acknowledgements

Financial support for this research by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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