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Preliminary communication

Electronic spectrum and photoreactivity of dimethyl(1,5-cyclooctadiene)-platinum(II)

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Abstract

The electronic spectrum of $Pt^{II}(COD)(CH_3)_2$ (COD = 1,5-cyclooctadiene) in CH_3CN shows two long-wavelength absorptions at $\lambda_{max} = 352$ nm ($\varepsilon = 150$) and 318 nm (790) which are assigned to the spin-forbidden and spin-allowed ligand-to-ligand charge transfer transitions $a_1 \rightarrow b_1$ ($CH_3^- \rightarrow \pi^*$ COD). The complex is non-emissive but photoreactive. While $Ph^{II}(COD)(CH_3)_2$ undergoes a photodecomposition in CH_3CN an oxidative addition takes place in the presence of CH_3I. The photoproduct $[Pt^{IV}(CH_3)_3I]_4$ is formed with $\phi = 0.005$ at $\lambda_{irr} = 313$ nm. © 1998 Elsevier Science S.A.

Keywords: Platinum complexes; Absorption spectra; Photochemistry

1. Introduction

Complexes of the type olefin–M–R are organometallic compounds which simultaneously contain an olefin as π-acceptor and a carbanion as rather strong σ-donor. Accordingly, a CT interaction between the donor and acceptor ligand mediated by the central metal is feasible. Such a CT interaction may lead to an electronic ligand-to-ligand charge transfer (LLCT) transition [1] which might appear as an absorption and emission band in the spectra of such complexes. Moreover, LLCT excitation could induce photochemical reactions which are characteristic for compounds of this composition. As an intriguing possibility LLCT excitation may result in an insertion which is a key step in olefin polymerization [2,3]:

In order to obtain relevant information on the electronic spectra and photoreactivity of olefin/alkyl mixed-ligand complexes we selected $Pt(COD)(CH_3)_2$ with COD = 1,5-cyclooctadiene for the present study. This compound is well characterized [4,5], thermally rather stable and commercially available (Aldrich, Strem). While the electronic spectra and photochemistry of this complex have not yet been investigated, the photolysis of $Pt(COD)(i\text{-}C_3H_7)_2$ was utilized for the synthesis of $Pt(COD)_2$ [6]. Unfortunately, electronic spectra were not recorded. However, the present study is facilitated by previous investigations of the electronic spectra of other COD complexes [7] such as $[MCl(COD)]_2$ [8], $[M(en)(COD)]^+$ [9] with M = Rh and Ir. In addition, the spectra and photochemistry of Pt(diimine)R_2 complexes have been described in some detail [10,11]. In this case diimines such as 2,2′-bipyridyl serve as acceptor ligand.

2. Results

The absorption spectrum of $Pt(COD)(CH_3)_2$ in CH_3CN (Fig. 1) shows bands at $\lambda_{max} = 352$ ($\varepsilon = 150$ dm^3 M^{-1} cm^{-1}), 318 (790), 286 (1340), 248 (2350) and 218 nm (10 000). For the purpose of comparison the spectrum of $Pt(COD)Cl_2$ in CH_3CN was also recorded. It displays two absorptions at $\lambda_{max} = 256$ (4100) and 218 nm (17 500). $Pt(COD)(CH_3)_2$ does not emit at room temperature or 77 K. However, the compound is light sensitive in solution. Upon irradiation with $\lambda_{irr} >$ 290 nm $Pt(COD)(CH_3)_2$ in CH_3CN underwent a photodecomposition as indicated by the concomitant spectral changes which included a general increase of the optical density over the entire absorption spectrum. This

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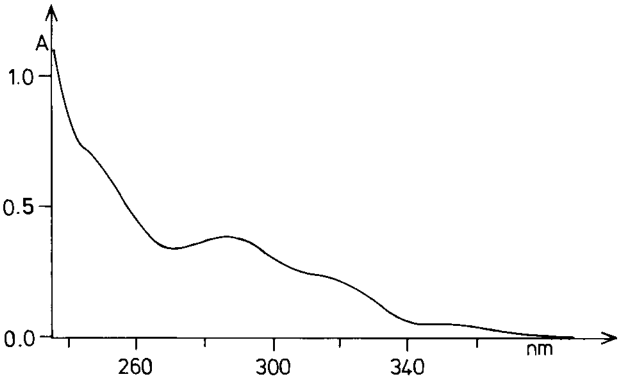

Fig. 1. Electronic absorption spectrum of 2.88×10^{-4} M $Pt(COD)(CH_3)_2$ at room temperature in acetonitrile, 1 cm cell.

effect is caused by the photochemical formation of colloidal particles which consist of elemental platinum. Upon addition of CH_3I ($\sim$ 0.1 M) $Pt(COD)(CH_3)_2$ is slowly converted to $[Pt(CH_3)_3I]_4$ in a thermal reaction [5]. The photolysis ($\lambda_{irr} > 290$ nm) of $Pt(COD)(CH_3)_2$ in CH_3CN in the presence of CH_3I ($\sim 10^{-3}$ M) led to the same product. At higher concentrations of $Pt(COD)(CH_3)_2$ ($\sim 10^{-2}$ M) the irradiation was accompanied by the precipitation of $[Pt(COD)(CH_3)_3I]_4$ which was identified by its characteristic emission spectrum ($\lambda_{max} = 735$ nm) [12]. The tetramer was formed with $\phi = 0.005$ at $\lambda_{irr} = 313$ nm.

3. Discussion

The absorption spectra of $[Ir(COD)Cl]_2$ [8], $[Ir(COD)en]^+$ [9] are characterized by two long-wavelength bands which were assigned to the lowest-energy ($a_1 \rightarrow b_1$, in C_{2v} symmetry) metal-to-ligand charge transfer (MLCT) transition terminating at the π^* orbitals of the diolefin ligand. The weaker band at longer wavelength belongs to a spin-forbidden transition while the more intense band at shorter wavelength is assigned to the corresponding spin-allowed transition. The singlet triplet separation between both transitions is approximately 3000 cm^{-1} [9]. It was noticed that MLCT bands of $Pt(COD)Cl_2$ appear at higher energies in agreement with the expectation. [1] In analogy to the iridium complexes we assign the longest-wavelength band of $Pt(COD)Cl_2$ at $\lambda_{max} = 256$ nm to the spin-allowed $a_1 \rightarrow b_1$ MLCT transition. A weaker ^{3}MLCT band at longer wavelength is not discernible but may be obscured by the ^{1}MLCT absorption.

The absorption spectrum of $Pt(COD)(CH_3)_2$ (Fig. 1) shows several bands including two long-wavelength absorptions at 318 nm ($\varepsilon = 790$) and 325 nm (150) which are separated by $\sim$ 3000 cm^{-1}. It is then tempting to assign these bands to the spin-allowed and spin-forbidden $a_1 \rightarrow b_1$ MLCT transition. However, there is no obvious reason why this MLCT transition should occur at lower energies than the corresponding MLCT transition of $Pt(COD)Cl_2$. A closer look at the electronic structure of $Pt(COD)(CH_3)_2$ provides a satisfactory explanation.

In contrast to chloride, alkyl ligands provide σ-bonding orbitals at rather high energies. Calculations of *cis*-$Pt(PH_3)_2(CH_3)_2$ have shown that the MOs which represent the platinum–carbon bonds (a_1 and b_2 in C_{2v} symmetry) are located above the non-bonding d orbitals of platinum [13]. Since the phosphine ligands are also π-acceptors this picture can be directly applied to $Pt(COD)(CH_3)_2$ without much modification (Fig. 2). Accordingly, the HOMO is an a_1 orbital with a large contribution from the methyl ligand while the LUMO is a b_1 orbital which consists of π^*(COD) and p_x of Pt. The lowest-energy transition $3a_1 \rightarrow 2b_1$ is of the same symmetry as the lowest-energy MLCT transitions of other COD complexes such as $Pt(COD)Cl_2$ or $Ir(COD)(CH_3)_2$. However, the $3a_1 \rightarrow 2b_1$ transition of $Pt(COD)(CH_3)_2$ occurs at lower energies when compared with $Pt(COD)Cl_2$ and is now of the LLCT type since it involves the promotion of an electron from the Pt–CH_3 bond to the π^*(COD) orbitals. In this context it is of interest that various mixed-ligand complexes which contain 1,2-diimine ligands and carbanions are also characterized by low-energy LLCT transitions

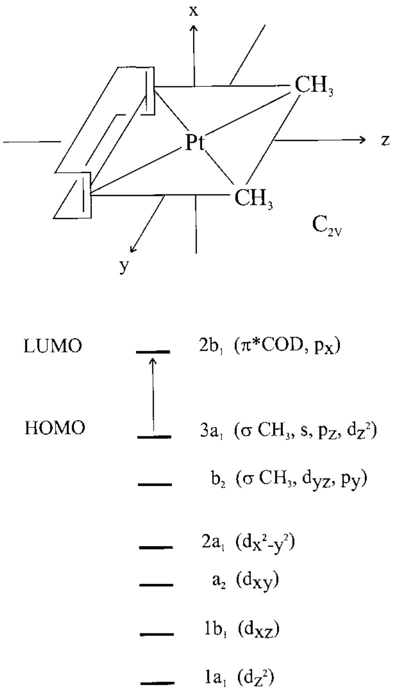

Fig. 2. MO diagram of $Pt(COD)(CH_3)_2$, adopted from Ref. [13].

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[1] See Ref. 21 in Ref. [8].

[1,14]. Such a LLCT assignment may also apply to the lowest-energy transition of Pt(diimine)$(CH_3)_2$ which, however, has been assumed to be of the MLCT type [10,11].

Other transitions of Pt(COD)$(CH_3)_2$ at higher energies include LLCT ($b_2 \rightarrow b_1$) and MLCT transitions ($1a_1$, $1b_1$, a_2, $2a_1 \rightarrow 2b_1$) type (Fig. 2). No attempt was made to identify the corresponding absorption bands. However, the very intense band at 218 nm is probably an intraligand absorption of COD which appears also in the spectrum of Pt(COD)Cl_2. The free COD ligand absorbs at $\lambda_{max} = 198$ nm.

While the MLCT states of COD complexes such as $[Ir(COD)en]^+$ are emissive [9] Pt(COD)$(CH_3)_2$ was not observed to emit. However, Pt(COD)$(CH_3)_2$ is light sensitive in solution. In CH_3CN the compound undergoes a photodecomposition. Although the products were not identified elemental platinum is apparently formed. It may be speculated that this observation can be attributed to the reactivity of a LLCT state. LLCT excitation could finally lead to the reduction of the metal and oxidation of CH_3^- ligands in analogy to methylcobalamin [15]. The photolysis of $Pt^{II}(COD)(i\text{-}C_3H_7)_2$ which yields $Pt^0(COD)_2$ in the presence of COD might be also induced by LLCT excitation [6].

In the presence of CH_3I the photolysis of Pt(COD)$(CH_3)_2$ leads to an oxidative addition:

$$Pt(COD)(CH_3)_2 + CH_3I \rightarrow 1/4\left[Pt^{IV}(CH_3)_3I\right]_4 + COD$$

Photooxidations with alkyl halides as oxidants were observed for a variety of Pt(II) complexes including Pt(*o*-phen)$(CH_3)_2$ [11], Pt(bipy)Cl_2 [16], $Pt(thpy)_2$ [17,18] (thpy = 2-(2-thienyl)-pyridine anion) and Pt(bipy)(tdt) (tdt^{2-} = 3,4-toluene-dithiolate) [19]. It seems that this photoreactivity cannot be attributed to a particular type of excited state since MLCT as well as LLCT states can induce photooxidations of Pt(II) complexes.

Acknowledgements

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