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Preliminary communication

Photolysis of the ion pair $[\eta^7\text{-}C_7H_7Mo(CO)_3]^+BPh_4^-$ induced by outer sphere 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 the ion pair $[\eta^7\text{-}C_7H_7Mo(CO)_3]^+BPh_4^-$ in CH_2Cl_2 shows an outer sphere charge transfer (OSCT) absorption at $\lambda_{max} = 370$ nm. OSCT excitation yields $[(\eta^6\text{-}C_7H_7Ph)Mo(CO)_3]$ with $\phi = 0.02$ at $\lambda = 405$ nm. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The intermolecular (outer sphere, OS) interaction between an oxidizing cation and a reducing anion generates a new optical transition involving charge transfer (CT) from the electron donor to the acceptor. Metal complexes as well as simple organic and inorganic ions form such ion pairs which show OSCT absorptions in their electronic spectra [1,2]. Although carbanions including $C_6H_5^-$ are quite reducing they are generally not suitable as electron donors in ion pairs owing to their nucleophilicity. However, the reactivity of $C_6H_5^-$ is attenuated when it is added to BPh_3. Ion pairs which consist of an oxidizing complex cation and BPh_4^- are well known to display OSCT absorptions [1–6]. The photooxidation of BPh_4 yields simply phenyl radicals and BPh_3. This photoreactivity may be utilized in organometallic chemistry. We explored this possibility and selected the salt $[\eta^7\text{-}C_7H_7Mo(CO)_3]BPh_4$ for the present study. This choice is based on the electron-accepting properties of the tropylium cation in the free and coordinated state. Ion pairs of the type $C_7H_7^+X^-$ are characterized by long-wavelength OSCT absorptions [7–9]. Moreover, it has been shown quite recently that the lowest-energy transition of $[\eta^7\text{-}C_7H_7Mo(CO)_3]^+$ involves metal to ligand charge transfer terminating at the tropylium ligand [10].

2. Results

The electronic spectrum of $[C_7H_7Mo(CO)_3]PF_6$ in CH_3CN shows absorptions at $\lambda = 380$ ($\varepsilon = 1200$ M^{-1} cm^{-1}), 298 (22400) and 236 nm (sh, 13600) [10]. When the anion PF_6^- is replaced by BPh_4^- the optical density slightly increases over the entire absorption spectrum of $[C_7H_7Mo(CO)_3]^+$ although BPh_4^- absorbs only below 290 nm. This increase is amplified when CH_2Cl_2 is used as solvent (Fig. 1). The difference spectrum of $[C_7H_7Mo(CO)_3]BPh_4$ in CH_3CN and CH_2Cl_2 reveals a new absorption maximum at $\lambda_{max} = 370$ nm ($\varepsilon = 2800$) in CH_2Cl_2. This absorption does not follow the Lambert–Beer law. The extinction coefficient decreases upon dilution. This behavior is typical for an absorption of an ion pair which dissociates in more polar solvents and at smaller concentrations.

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

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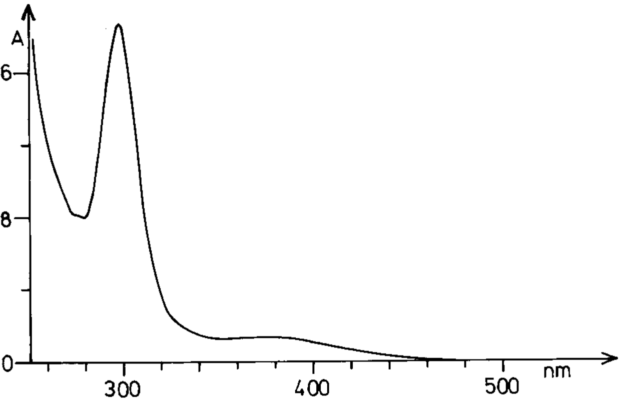

Fig. 1. Electronic absorption spectrum of 5.60×10^{-5} M $[C_7H_7Mo(CO)_3]BPh_4$ in CH_2Cl_2 under argon at room temperature, 1 cm cell.

The salt $[C_7H_7Mo(CO)_3]PF_6$ is slightly light sensitive in various solvents including CH_2Cl_2. However, the photolysis is negligible if the wavelength of irradiation is larger than 390 nm. In contrast to the hexafluorophosphate, $[C_7H_7Mo(CO)_3]BPh_4$ is still quite photoactive at $\lambda_{irr} > 390$ nm. The concomitant spectral changes (Fig. 2) are rather clear in the beginning, but are obscured by a secondary photolysis at later stages. The spectral variations during the first part of the photolysis are duplicated when LiPh is added to solutions of $[C_7H_7Mo(CO)_3]BPh_4$. Nucleophilic anions X react with $[C_7H_7Mo(CO)_3]^+$ to yield $[(C_7H_7X)Mo(CO)_3]$ [11,12]. The addition of Ph^- leads to the generation of $[(C_7H_7Ph)Mo(CO)_3]$ which contains phenylcycloheptatriene as a ligand. This assumption is corroborated by an analysis of the spectral changes. The absorption spectrum of $[(C_7H_7Ph)Mo(CO)_3]$ is quite similar to that of $[C_7H_8Mo(CO)_3]$ ($\lambda_{max} = 486$ nm). Phenyl substitution at the cycloheptatriene ligand has apparently only a small effect on the absorption spectrum of the complex.

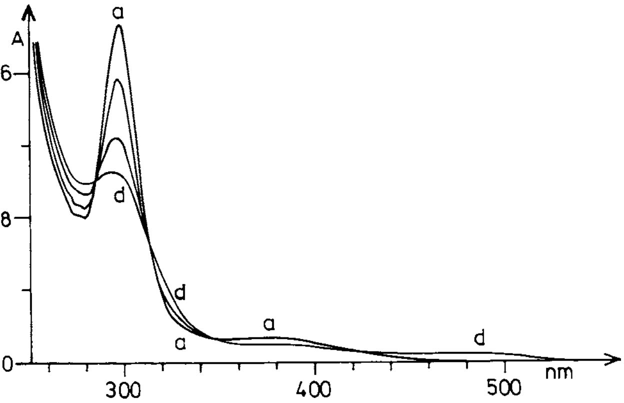

Fig. 2. Spectral changes during the photolysis of 5.60×10^{-5} M $[C_7H_7Mo(CO)_3]BPh_4$ in CH_2Cl_2 under argon at room temperature after 0 (a) and 1, 2 and 4 (d) min irradiation time with $\lambda_{irr} = 405$ nm (Xe/Hg 977 B-1 lamp), 1 cm cell.

3. Discussion

It is well known that the thermal reaction of $[C_7H_7Mo(CO)_3]^+$ with nucleophiles such as carbanions leads to an addition which yields cycloheptatriene complexes [11,12]:

$$[\eta^7\text{-}C_7H_7Mo(CO)_3]^+R^- \rightarrow [(\eta^6\text{-}C_7H_7R)Mo(CO)_3]$$

In contrast to the ion pair $[\eta^7\text{-}C_7H_7Mo(CO)_3]^+Ph^-$, the salt $[\eta^7\text{-}C_7H_7Mo(CO)_3]BPh_4$ is sufficiently stable and does not react according to the equation:

$$[\eta^7\text{-}C_7H_7Mo(CO)_3]^+BPh4^- \rightarrow [(\eta^6\text{-}C_7H_7Ph)Mo(CO)_3] + BPh_3$$

The reactivity of the phenyl anion is apparently diminished or eliminated if it is added to BPh_3. However, the electron-donating character of Ph^- is still partially preserved in BPh_4^-. The electronic spectrum of the ion pair $[C_7H_7Mo(CO)_3]^+BPh_4^-$ show an new absorption at $\lambda_{max} = 365$ nm which is attributed to an OSCT transition from BPh_4^- to $[C_7H_7Mo(CO)_3]^+$. Since the coordinated tropylium serves as electron acceptor [10] CT excitation should generate a radical pair in the primary photochemical step:

$$[(C_7H_7^+)Mo(CO)_3] + BPh_4^- \xrightarrow{h\nu} [(C_7H_7^\bullet)Mo(CO)_3]Ph^\bullet + BPh_3$$

Finally, radical coupling yields the stable photoproduct $[(\eta^6\text{-}C_7H_7Ph)Mo(CO)_3]$ which contains phenylcycloheptatriene as triolefin ligand.

In summary, the photoreactivity of a redoxactive ion pair containing BPh_4^- was used to covalently add the phenyl anion to a suitable complex cation. This photoreaction may find more applications in organometallic chemistry.

Acknowledgements

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