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Photochemistry induced by metal-to-ligand charge transfer excitation

Arnd Vogler *, Horst Kunkely

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

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Abstract

The photoreactivity of coordination compounds in a MLCT excited state can be attributed to the nature of the oxidized metal and/or the reduced ligand. The general features of such photoreactions have been recently reviewed (A. Vogler, H. Kunkely, Coord. Chem. Rev. 177 (1998) 81). The present report contains an update of our observations on this subject. In particular, the spectroscopy and photochemistry of the following complexes is discussed: $[Re^{I}(CO)_4S_2COEt]$, $[Fe^{II}(CN)_5ONPh]^{3-}$, $[(C_7H_7)Mo^{0}(CO)_3]^{+}$, $[Fe_2(CO)_6S_2]$, $Pd^{0}[(PPh_2\text{-}C_5H_4)_2Fe^{II}]_2$, $Rh^{I}(PPh_3)_2(CS)Cl$ and $[(i\text{-}C_3H_7C_5H_4)_2WH_2]\cdot$9,10-phenanthrenequinone.

Keywords: Photochemistry; Charge transfer

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* Corresponding author. Tel.: +49-941-9434485; fax: +49-941-9434488.
E-mail address: arnd.vogler@chemie.uni-regensburg.de (A. Vogler).

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1. Introduction

Coordination compounds such as $Ru(bipy)_3^{2+}$ [1–3] or $Re(bipy)(CO)_3Cl$ [3–6] are considered to be prototype examples for the properties of metal-to-ligand charge transfer (MLCT) excited states. In these cases MLCT states are luminescent and not intrinsically reactive. However, in contrast to these examples, there is increasing evidence that a variety of other complexes are characterized by reactive MLCT states. We have recently reviewed this subject [7], and present now a summary of new photoreactions we observed upon MLCT excitation.

In a very simple approach, a complex in a MLCT state can be viewed as an isomer of the ground state which contains an oxidized metal and reduced ligand. The excited state reactivity can then be ascribed to the nature of the oxidized metal center or/and reduced ligand. According to this picture the following classification is appropriate.

Frequently, the reactivity of MLCT states is based on the oxidation of the metal. Subsequent processes include associative ligand substitution, exciplex formation and cleavage of metal–metal bonds.

The reactivity of MLCT states may originate from the reduced ligand. Photoreactions of this type include dissociative ligand substitution, ligand isomerization, ligand fragmentation, electrophilic attack and radical reactions at the reduced ligand. Moreover, ligand reduction may also result in an oxidative addition. MLCT states of the $d \rightarrow \pi^*$ as well as $d\sigma^*$ type can induce such intramolecular redox reactions.

Finally, there are outer sphere charge transfer (OSCT) excitations [8,9] which are related to MLCT. In this case the acceptor is a second sphere ligand. Any suitable compound which serves as an intermolecular acceptor for a reducing metal center may show this type of OSCT interaction. If the acceptor is the solvent the corresponding OSCT transitions are termed, charge transfer to solvent (CTTS). Photooxidations of the metal complexes and irreversible reductions of the acceptors result from such OSCT excitations.

In the following discussion we summarize our recent observations on the photoreactivity of MLCT excited states. Some reactions described are based on ligand reductions. In addition, novel examples of reactive OSCT states which are related to MLCT states are also discussed below.

2. Reactivity of MLCT states based on the reduction of ligands

2.1. Irreversible ligand reduction/ligand fragmentation

The photolysis of $Cu^{I}(PPh_3)_2NO_3$ [10] leads to the formation of $Cu^{II}(PPh_3)_2O$ and NO_2 in the primary photochemical step. It has been suggested that this photoredox reaction is induced by $Cu^{I} \rightarrow NO_3^-$ MLCT excitation. The carbonate is isoelectronic to the nitrate and another potential acceptor for a MLCT transition. A concomitant photoreduction of CO_3^{2-} would be of considerable interest with regard to solar energy conversion and a decrease of the current CO_2 level. However, carbonate is hardly oxidizing and MLCT transition terminating at the π^* orbital of CO_3^{2-} may occur only at very high energies. The electron accepting properties of carbonate or esters of carbonic acid might improve if oxygen is substituted by sulfur because the π^* orbitals of the planar ligand drop to lower energies as a consequence of weaker C–S π-bonding. Accordingly, trithiocarbonate or xanthate (CS_2OR^-) complexes with reducing metals should be suitable candidates for the detection of MLCT absorptions and possibly photochemical reduction of such ligands.

The complex $Re^I(CO)_4S_2COEt$ shows a long-wavelength absorption at 327 nm which is assigned to a MLCT transition terminating at the π^* orbital of the xanthate ligand [11]. The complex is not luminescent but photoreactive. MLCT excitation leads to the decomposition of the compound. The concomitant spectral variations do not show a uniform pattern indicating the occurrence of secondary and side reactions. Generally, with the exception of excited state electron transfer, Re^I carbonyl complexes do not undergo photoreactions induced by MLCT excitation [3–6]. In the case of the xanthate complex, it is concluded that the photoreactivity is based on the reduction of xanthate in the MLCT excited state.

2.2. Electrophilic attack at the reduced ligand

In a MLCT excited state, the electron density at the ligand is increased. Consequently, the ligand should be susceptible to an electrophilic attack. Typical examples of this type are the photoreactions of the complexes $Co^{-1}(CO)_3NO$ [12] and $Os^0(CPh)(CO)(P\phi_3)_2Cl$ [13] which are characterized by low-energy MLCT transitions terminating at the nitrosyl and carbyne ligands, respectively. In the MLCT excited states, these ligands are attacked by protons. In the case of the carbyne complex, MLCT excitation is simply followed by the addition of HCl and the formation of the carbene complex $Os(CHPh)(CO)\ (P\phi_3)_2Cl_2$.

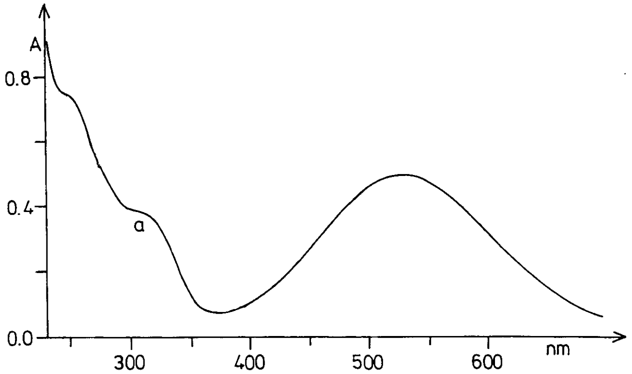


Fig. 1. Electronic absorption spectrum of 9.38×10^{-5} M $[Fe(CN)_5(ONPh)]^{3-}$ in water at room temperature (r.t.), in a 1 cm cell.

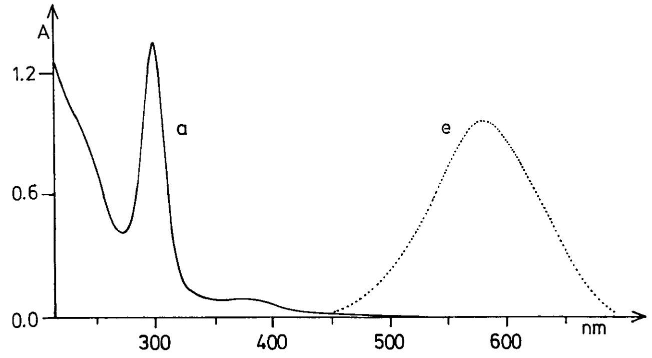


Fig. 2. Electronic absorption (—) and emission (…) spectra of $[(\eta\text{-}C_7H_7Mo(CO)_3]PF_6$ at r.t. under argon. Absorption: 5.63×10^{-5} M in EtOH, in a 1 cm cell. Emission: in CH_3CN, $\lambda_{exc} = 380$ nm, intensity in arbitrary units.

Recently, we observed a related photoreaction. The anion $[Fe^{II}(CN)_5(ONPh)]^{3-}$ displays an intense band at $\lambda_{max} = 528$ nm (Fig. 1) which is attributed to a MLCT transition from Fe^{II} to a π^* orbital of the nitrosobenzene ligand [14]. Upon MLCT excitation the photolysis proceeds according to the equation:

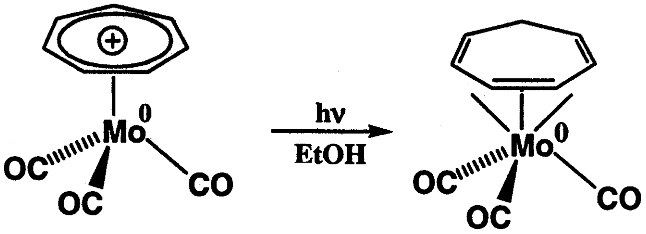
$$[Fe(CN)_5ONPh]^{3-} + H^+ \rightarrow [Fe(CN)_5NO]^{2-} + C_6H_6$$

It is suggested that in the MLCT excited state, the reduced nitrosobenzene is attacked by a proton generating the complex $[Fe^{III}(CN)_5(ONHPh)]^{2-}$. The ligand ONHPh is apparently not stable but decomposes to benzene and NO. Finally, NO recombines with $[Fe^{III}(CN)_5]^{2-}$ to generate the nitroprusside complex.

It should be emphasized that this photoreaction provides a new access to nitrosyl complexes which are of considerable interest with regard to the biological role of NO [15,16].

2.3. Radical reactions at the reduced ligand

In the MLCT state, a ligand is reduced to a radical. Consequently, typical radical reactions may be observed following MLCT excitation. The photoreactivity of $[C_7H_7Mo^0(CO)_3]^+$ seems to belong to this category. This cation shows a longest-wavelength absorption at $\lambda_{max} = 379$ nm which is assigned to a Mo^0 to $C_7H_7^+$ MLCT transition [17] (Fig. 2). The MLCT excited state is not only luminescent at



room temperature ($\lambda_{max} = 580$ nm) but also reactive. In ethanol, $[C_7H_7Mo^0(CO)_3]^+$ is photoreduced to $[C_7H_8Mo^0(CO)_3]$.

This reaction consists of a hydride transfer from ethanol to the tropylium ligand yielding the cycloheptatrien complex and acetaldehyde. The mechanism can be rationalized by the following considerations. In the MLCT excited state, the complex contains Mo^I and a C_7H_7 radical which should be able to abstract a hydrogen atom from ethanol:

$$[(C_7H_7^+)Mo^0(CO)_3]^+ \xrightarrow{h\nu} [(^{\bullet}C_7H_7^+)Mo^I(CO)_3]^+$$

$$[(^{\bullet}C_7H_7)Mo^I(CO)_3]^+ + C_2H_5OH \rightarrow [(C_7H_8)Mo^I(CO)_3]^+ + CH_3(^{\bullet}CH)OH$$

The $CH_3(^{\bullet}CH)OH$ radical is a strong reductant and transfers an electron to the oxidizing Mo^I complex yielding the final products.

2.4. Ligand reduction resulting in oxidative addition

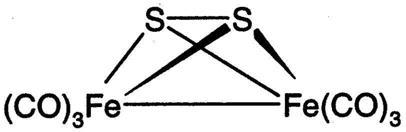
Oxidative additions take place by a reductive cleavage of a σ-bond. Two electrons are transferred from a metal to a suitable substrate which yields two anions. These are added as ligands to the oxidized metal:

$$M^{n+} + A\text{–}A' \rightarrow A\text{–}M^{n+2}\text{–}A'$$

Photoreactions of this class should be induced by CT excitation from M^{n+} into the σ^* orbital of A–A′. If A–A′ coordinates to M^{n+} the absorption spectrum of $M^{n+}(A\text{–}A')$ may display a $d\sigma^*$ MLCT band. The appearance of such MLCT bands at long wavelengths require ligands with low-energy σ^* orbitals such as O_2^{2-} or RSe–SeR [18]. The binuclear ligand-bridged complex $Re_2^IBr_2(CO)_6(Se_2Ph_2)$ shows a $d\sigma^*$ MLCT absorption at $\lambda_{max} = 434$ nm [19]. Upon MLCT excitation, the compound decomposes. It was suggested that the primary photochemical step is an oxidative addition:

$$Re_2^I(Se_2Ph_2) \xrightarrow{h\nu} 2Re^{II}(SePh^-)$$

Although photoproducts have not yet been identified, the reductive splitting of the Se–Se σ bond seems to be a reasonable assumption. In a search for further examples of reactive $d\sigma^*$ MLCT states, we explored $Fe_2S_2(CO)_6$ [20].



This complex is well known to be light sensitive. It undergoes photoreactions, such as dimerization and addition to carbon–carbon double bonds. On the basis of structural data and MO calculations, $Fe_2S_2(CO)_6$ can be described roughly as a complex with a bridging disulfide ligand and a metal–metal bond which connects two Fe^I d^7 centers. The HOMO is represented by the Fe–Fe σ-bond while the LUMO is antibonding with regard to the S–S bond. The longest wavelength absorption of $Fe_2S_2(CO)_6$ near 460 nm (Fig. 3) is then assigned to a dσ^* transition terminating at the bridging disulfide ligand [20]. MLCT excitation should lead to an oxidative addition:

$$Fe_2^I(S_2^{2-})(CO)_6 \xrightarrow{h\nu} 2Fe^{II}(S^{2-})(CO)_3$$

These coordinatively unsaturated fragments add, apparently, to an intact $Fe_2S_2(CO)_6$ molecule in its ground state and $Fe_4S_4(CO)_{12}$ is formed as the final photoproduct.

In this context it should be emphasized that the excited state properties of $Fe_2S_2(CO)_6$ should be also of interest in the field of bioinorganic chemistry since iron–sulfur clusters constitute an important family of metallo enzymes.

3. Outer sphere charge transfer (OSCT) excitation related to MLCT

Related to MLCT are CT transitions from a metal center to an acceptor which is not bonded but located in close contact to the metal [8,9]. If the electronic coupling is strong enough, optical OSCT terminating at second sphere ligands can occur. Frequently, the solvent serves as acceptor and the corresponding transition appears as a CTTS absorption. A typical example is represented by ferrocene which in chlorinated alkanes, such as CCl_4 shows such a CTTS band [4,21,22]. Upon CTTS excitation ferrocene undergoes an oxidation to the ferrocenium cation:

$$Fe^{II}(C_5H_5)_2 + R\text{–}Cl \rightarrow [Fe^{III}(C_5H_5)_2]^+Cl^- + R^\bullet$$

This photoreaction is irreversible because R–Cl decays upon reduction. An interesting variation of this process is observed when $Pd^0[(PPh_2C_5H_4)_2Fe^{II}]_2$ is photolyzed in CCl_4 [23]. The trinuclear complex dissolved in CCl_4 shows a new absorption at $\lambda_{max} = 338$ nm (Fig. 4) which appear at almost the same wavelength as the corresponding band of ferrocene in CCl_4. Accordingly, the new absorption of

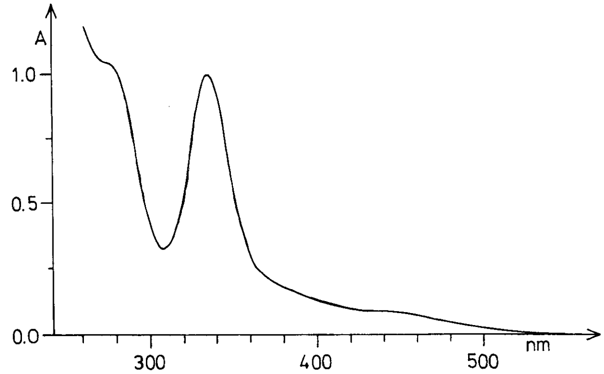


Fig. 3. Electronic absorption spectrum of 8.9×10^{-5} M $Fe_2S_2(CO)_6$ in CH_3CN under argon at r.t., in a 1 cm cell.

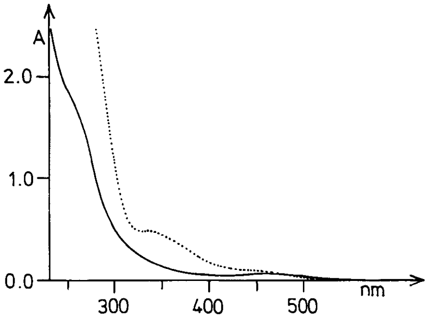
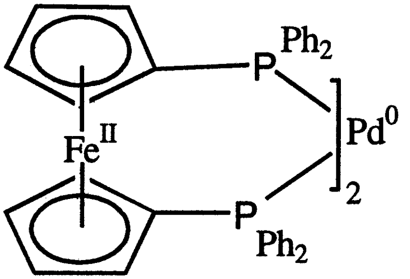


Fig. 4. Electronic absorption spectra of 5.47×10^{-5} M $Pd(BDPF)_2$ in CH_3CN (—) and CCl_4 (...) at r.t., in a 1 cm cell.



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the trinuclear complex is also assigned to a ferrocene to CCl_4 CTTS transition. CTTS excitation of the trinuclear complex leads then, certainly to the photooxidation of Fe^{II} in the primary photochemical step. However, the ferrocenium cation is apparently able to oxidize Pd^0. The complete mechanism may be described by the following scheme:

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

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

$$2Pd^I[(PPh_2C_5H_4)_2Fe^{II}]_2^+Cl^- \rightarrow Pd^0[(PPh_2C_5H_4)_2Fe^{II}]_2 + Pd^{II}[(PPh_2C_5H_4)_2Fe^{II}]Cl_2 + [(PPh_2C_5H_4)_2Fe^{II}]$$

In summary, the outer sphere photooxidation of the ferrocene moiety is followed by a facile intramolecular electron transfer from Pd^0 to Fe^{III} which finally leads to Pd^{II} via disproportionation of Pd^I. This novel photoredox process represents a special type of photoinduced electron transfer in polynuclear complexes and may be important for applications in supramolecular photochemistry.

OSCT transitions originating from a metal center may not only terminate at the solvent but also at other acceptors [8]. This type of OSCT is observed in the electronic spectrum of the addition compounds of $(C_5H_5)_2MH_2$ (M = Mo and W) and a variety of neutral acceptors such as olefins with electron-withdrawing substituents [24]. The addition compound $(i\text{-}C_3H_7C_5H_4)_2WH_2 \cdot$9,10-phenanthrenequinone displays the longest-wavelength absorption at $\lambda_{max} = 530$ nm (Fig. 5) which is assigned to an OSCT transition from the hydride complex to the quinone [25]. While hydride complexes undergo, simply a photochemical release of H_2 [4]; OSCT excitation of the addition compound leads to a hydrogen transfer from the complex to the quinone:

$$(i\text{-}C_3H_7C_5H_4)_2W + \text{9,10-phenanthrenequinone} \xrightarrow{h\nu} (i\text{-}C_3H_7C_5H_4)_2W + \text{9,10-phenanthrenediol}$$

This reaction is certainly facilitated by the OSCT transition which involves an oxidation of the complex and reduction of the quinone. Product formation occurs then by the transfer of protons from the oxidized complex to the reduced quinone. Of course, the overall photoreaction may not proceed via well-defined intermediates but also as a concerted process. In summary, this photoreaction seems to be the first example of a photoinduced hydrogen transfer which utilizes a hydride complex as a hydrogen donor.

In the case of the two previous examples, it is quite obvious that the photoreactions are initiated by optical CT. However, the reduction of an external acceptor may also take place when an OSCT absorption is not observed [7]. It is feasible that OSCT bands are present but obscured by more intense absorptions of different origins. As an alternative, an excited state electron transfer mechanism could induce such photoredox reactions. Various photooxidations of metal complexes in halocarbon solvents belong to this category [7]. In this context we have studied recently, the compound $Rh^I(PPh_3)_2(CS)Cl$ [26]. This complex is characterized by a low-energy MLCT transition which terminates at the π^* orbitals of the thiocarbonyl ligand. In solution of CH_2Cl_2 a light-induced oxidative addition takes place:

$$Rh^I(PPh_3)_2(CS)Cl + 2CH_2Cl_2 \rightarrow Rh^{III}(PPh_3)_2(CS)Cl_3 + 2^\bullet CHCl_2$$

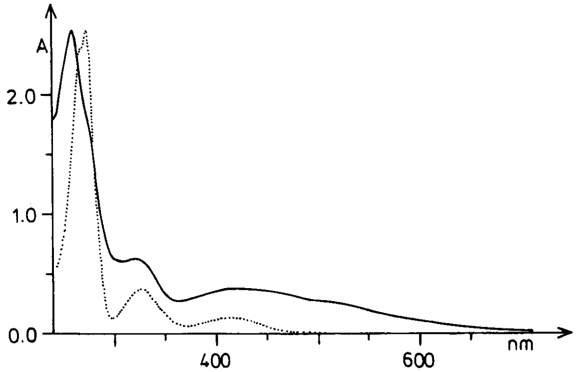

Fig. 5. Electronic absorption spectra of 8.28×10^{-5} M phenanthrenequinone (...) and 5.65×10^{-5} M $(i\text{-}C_3H_7C_5H_4)_2WH_2 \cdot$9,10-phenanthrenequinone (—) in CH_2Cl_2 at r.t., in a 1 cm cell.

This photooxidation occurs when the light is absorbed by the long-wavelength MLCT ($Rh^{I} \rightarrow CS$) band. In the excited state, the reduced thiocarbonyl ligand apparently transfers its excess electron to the solvent in the primary photochemical step. In contrast to the thiocarbonyl complex, the analogous carbonyl compound, $Rh^{I}(PPh_3)_2(CO)Cl$ shows a quite different behavior. Since the CO ligand does not provide π^* orbitals at rather low energies, a LF state is now the lowest-energy state of the complex. Accordingly, the complex simply undergoes a photorelease of the CO ligand.

Acknowledgements

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