

Electronic spectra and photoreactivity of cyclopentadienyl complexes

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Contents

Abstract	223
1. Introduction	224
2. Metal-centered excited states	225
3. Intraligand excited states	226
4. Ligand-to-metal charge transfer excited states	227
5. Metal-to-ligand charge transfer excited states	228
6. Ligand-to-ligand charge transfer excited states	228
7. Metal-to-metal charge transfer excited states	230
8. Outer sphere charge transfer excited states	230
9. Conclusion	232
Acknowledgements	232
References	232

Abstract

The cyclopentadienyl (Cp) ligand coordinates to high- and low-oxidation state transition metals as well as main group metals. Consequently, a variety of different excited states and photoreactions is possible. This diversity is illustrated by selected examples. Recent observations are emphasized. Spectral and photochemical properties are related to the following electronic transitions: metal-centered (e.g. Cp_2NbCl_2 , TiCp), intraligand, ligand-to-metal charge transfer (e.g. CpReO_3 , CpTiCl_3 , Cp_2TiS_5 , TiCp), metal-to-ligand charge transfer, ligand-to-ligand charge transfer (e.g. $\text{Cp}_2\text{Zr-2,2'-biquinoline}^{2+}$), metal-to-metal charge transfer (e.g. $\text{Cp}_2\text{Ti}[\text{NCRu}(\text{CN})_5]_2^{6-}$), outer sphere charge transfer (e.g. $\text{CoCp}_2^+\text{Mn}(\text{CO})_5^-$,

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CpWH₂ × 9,10-phenanthrenequinone) and charge-transfer-to-solvent. The Cp ligand may be directly involved in these electronic transitions or act as a spectator ligand. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electronic spectra; Photoreactivity; Cyclopentadienyl complexes

1. Introduction

Cyclopentadienyl (Cp) complexes play a very important role in organometallic chemistry. This ligand is known to coordinate to main group as well as transition metals in low- and high-oxidation states. Accordingly, a variety of different excited states and photochemical reactions is feasible. Various criteria can be applied to distinguish photochemical reactions. We found it convenient and useful to classify coordination compounds according to the nature of the photoreactive excited state because a certain type of electronic transition leads to the same consequences irrespective of a specific compound [1]. Photochemical reactions may thus be attributed to following excited states:

- metal-centered (MC);
- ligand-centered or intraligand (LC or IL);
- ligand-to-metal charge transfer (LMCT);
- metal-to-ligand charge transfer (MLCT);
- ligand-to-ligand charge transfer (LLCT);
- metal-to-metal charge transfer (MMCT);
- intraligand charge transfer (ILCT).

Generally, the aromatic Cp[−] anion coordinates as a pentahapto ligand (this applies to all Cp complexes discussed in this article) and provides its three pairs of π-electrons for σ-bonding to the metal. Accordingly, Cp[−] occupies three coordination sites in the complex. Back-bonding from the metal to the π*-orbitals of Cp[−] seems to be less important since these π*-orbitals occur at rather high energies [2].

The Cp[−] ligand may be directly involved in electronic transitions or simply act as spectator ligand. Cp[−] itself can participate in IL, LMCT, MLCT and LLCT transitions. However, π–π* IL transitions of the Cp[−] ligand occur at high energies [3] and have been rarely identified in the electronic spectra of Cp complexes (M⁺Cp[−] with M = Li, Na, K; λ_{max} < 200 nm) [3,4]. Cp[−] is a relatively strong electron donor owing to the high energy of its filled π-orbitals [2]. This notion is supported by the fact that this ligand is able to stabilize high-oxidation states. Accordingly, low-energy LMCT and LLCT transitions are of importance for Cp complexes. On the other side, the high energy of the π* orbitals of Cp[−] [2] do not favor low-energy MLCT transitions. Of course, the presence of MC and MMCT transitions does not require any particular ligand but their energies are also modified by Cp[−] as a spectator ligand.

The spectroscopy [2,5] and photochemistry [6,7] of various homoleptic Cp complexes (metallocenes) and some of their derivatives (e.g. ferrocene, Cp₂MX₂

with $M = \text{Ti, Zr}$) has been studied in quite some detail several decades ago. Mixed ligand cyclopentadienyl carbonyl complexes also played an important role in the development of organometallic photochemistry [6,7]. Some of these compounds will be mentioned in the present article in order to illustrate the diversity of excited states and photoreactions of Cp complexes. However, for a comprehensive treatment of this subject the reader is referred to previous publications. In our short review we emphasize some recent trends, in particular our own research.

2. Metal-centered excited states

Ferrocene and the cobaltocenium cation are typical examples of metallocenes with lowest-energy ligand-field (LF) excited states [2,5,8,9]. The longest-wavelength spin-allowed LF absorptions appear at $\lambda_{\text{max}} = 440$ nm for FeCp_2 and 404 nm for CoCp_2^+ . The ^3LF state of ferrocene can be populated from triplet excited states of organic compounds by energy transfer [6,7]. While FeCp_2 and CoCp_2^+ are not luminescent, the LF triplet of RuCp_2 is emissive at low temperatures [6,10–12]. The phosphorescence spectrum is highly structured with $\lambda_{\text{max}} \sim 625$ nm. LF excitation of these metallocenes does not lead to a photosubstitution. The reason for this photostability is not quite clear, but an electrostatic attraction between Cp^- and M^{n+} could retard a dissociative substitution. This assumption is supported by the observation that the complexes $[\text{CpM}^{\text{II}}(\text{arene})]^+$ with $M = \text{Fe}$ and Ru undergo a facile photosubstitution upon LF excitation [13,14]. In this case the neutral arene is substituted by a nucleophilic solvent.

We have recently examined the electronic spectra of $\text{Cp}_2\text{Nb}^{\text{IV}}\text{Cl}_2$ (Fig. 1) and $[\text{Cp}_2\text{Nb}^{\text{IV}}(\text{bipy})]^{2+}$ [15]. The longest-wavelength absorptions at $\lambda_{\text{max}} = 340$ and 350 nm, respectively, are attributed to LF transitions. Both complexes are luminescent at 77 K. The emission of Cp_2NbCl_2 appears at $\lambda_{\text{max}} = 620$ nm (Fig. 1) and of $[\text{Cp}_2\text{Nb}(\text{bipy})]^{2+}$ at 598 nm. This luminescence is a rare case of a LF emission of a

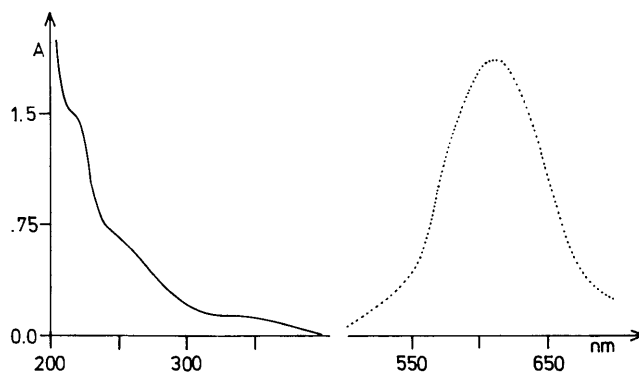


Fig. 1. Electronic absorption (—) and emission (....) spectrum of Cp_2NbCl_2 . Absorption: in CH_3CN , 1.29×10^{-4} M, at room temperature in a 1-cm cell. Emission: in EtOH, at 77 K, $\lambda_{\text{exc}} = 350$ nm; intensity in arbitrary units.

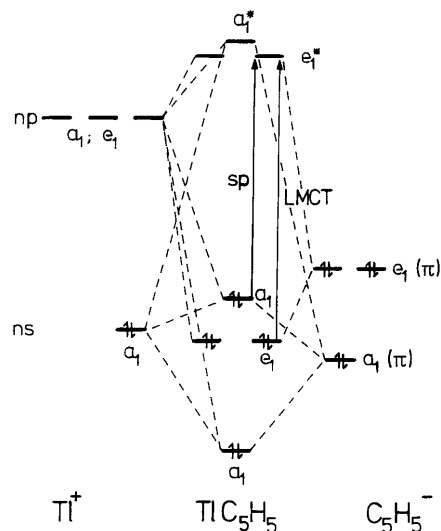


Fig. 2. Qualitative MO scheme of TlC_5H_5 (C_{5v} symmetry).

d^1 complex. Since the ground and lowest excited states are spin doublets the lowest-energy LF transitions in absorption and emission are spin-allowed processes.

Cp ligands not only coordinate to transition metals but also to Main Group metals. In particular, Cp complexes with s^2 metal ions such as Ga^+ , In^+ , Tl^+ , Ge^{2+} , Sn^{2+} , Pb^{2+} , Sb^{3+} and Bi^{3+} are well known [16–18]. Surprisingly, the electronic spectra and photochemistry of these compounds were not been studied until 1993. For an initial investigation we selected the complex TlCp [19], which is rather stable, easily accessible and structurally simple. The thallium cation forms the apex of a pyramid with Cp^- as the base. The electronic structure of TlCp is closely related to that of other s^2 complexes which carry three ligands (e.g. MCl_3^- with $\text{M} = \text{Ge}, \text{Sn}$ and Pb). All these complexes are characterized by low-energy MC sp transitions [20,21]. A qualitative MO scheme (Fig. 2) shows that the HOMO of TlCp contains a large contribution from the s-orbital of Tl while the LUMO is essentially composed of Tl p-orbitals [19]. Accordingly, the longest-wavelength absorption ($\lambda_{\text{max}} = 280$ nm) and emission ($\lambda_{\text{max}} = 360$ nm) are assigned to an sp transition. The luminescence of many halide complexes of s^2 metals originates also from sp excited states [20,21].

3. Intraligand excited states

As mentioned in the introduction IL transitions involving the Cp^- ligand do not occur at low energies [3,4]. However, in mixed ligand complexes an additional ligand may provide IL transitions at low energies. Mann and his group studied compounds of the type $\text{CpRu}^{\text{II}}\text{L}$ with $\text{L} = \text{e.g. coumarin}$ and rubrene [22,23]. These

highly emissive laser dyes preserve their long-wavelength absorptions in the coordinated state. Under certain conditions the coordinated dyes are also luminescent, but the structures of these labile species are not known, although reasonable proposals have been made.

4. Ligand-to-metal charge transfer excited states

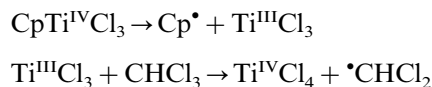
Since Cp^- is a relatively strong electron donor LMCT transitions occur at low energies provided the metal is oxidizing [2,5,8,9]. A suitable example is the ferrocenium cation. The intense blue color of $\text{Fe}^{\text{III}}\text{Cp}^{2+}$ is caused by the presence of a long-wavelength LMCT absorption ($\lambda_{\text{max}} = 617 \text{ nm}$).

Complexes with a d^0 configuration contain a transition metal in its highest possible oxidation state. Since no valence electrons are left at the metal only LMCT transitions may occur in simple complexes of this type. The compounds $(\text{C}_5\text{R}_5)\text{ReO}_3$ with $\text{R} = \text{H}$, alkyl are well-documented examples [24]. The longest-wavelength absorption of CpReO_3 at $\lambda_{\text{max}} = 372 \text{ nm}$ is assigned to a $\text{Cp}^- \rightarrow \text{Re}^{\text{VII}}$ LMCT transition. This band undergoes a red shift if the hydrogen atoms at the Cp ligand are replaced by electron-donating alkyl groups. The complex $(\text{C}_5\text{Me}_5)\text{ReO}_3$ shows its LMCT absorption at $\lambda_{\text{max}} = 402 \text{ nm}$. LMCT excitation of $(\text{C}_5\text{R}_5)\text{ReO}_3$ generates a radical pair in the primary photochemical step [24]:



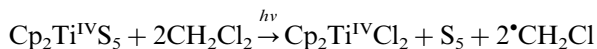
The C_5R_5 radical can be intercepted by suitable scavengers. As a competing process, recombination, takes place, which is favored with the increasing stability of the radical $\text{C}_5\text{R}_5^\bullet$. Since this stability increases in the series $\text{C}_5\text{H}_5 > \text{C}_5\text{H}_4\text{Me} > \text{C}_5\text{Me}_5$ the quantum yield of product formation drops in this direction. The radicals C_5R_5 are intercepted by hydrogen abstraction from the solvent or by dimerization.

Complexes of the type Cp_2MX_2 with the d^0 metals Ti(IV) and Zr(IV) are well known to be light sensitive upon LMCT excitation [6,25]. Recently, we have studied the photochemistry of CpTiCl_3 , which shows a $\text{Cp}^- \rightarrow \text{Ti}^{\text{IV}}$ LMCT absorption at $\lambda_{\text{max}} = 382 \text{ nm}$ [26]. LMCT excitation in CHCl_3 as the solvent leads to product formation according to the following equations:



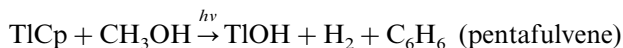
The generation of TiCl_4 takes place with $\phi = 0.003$ at $\lambda_{\text{irr}} = 405 \text{ nm}$. The recombination may be quite efficient in this case.

When X^- in Cp_2MX_2 is a stronger electron donor than Cp^- , LMCT transitions from X^- to $\text{M}(\text{IV})$ become the lowest energy transitions. This is illustrated by the complex Cp_2TiS_5 , which shows an intense LMCT absorption ($\text{S}_5^{2-} \rightarrow \text{Ti}^{\text{IV}}$) at $\lambda_{\text{max}} = 492 \text{ nm}$ [27]. The light sensitivity of Cp_2TiS_5 is now based on this electronic transition. LMCT excitation does not affect the Cp-M but the M-S_5 bond. In CH_2Cl_2 the photolysis proceeds according to the following stoichiometry:



The elemental sulfur appears finally in its most stable form S_8 .

LMCT involving Cp^- as donor ligand is not restricted to transition metals. Oxidizing main group metals are also suitable electron acceptors. For example, CpTi shows a LMCT absorption at $\lambda_{\text{max}} = 228 \text{ nm}$ in addition to the metal-centered sp band at $\lambda_{\text{max}} = 280 \text{ nm}$ (see above) [19]. While the sp state is emissive the LMCT state is reactive. In methanol product formation occurs according to the following equation:



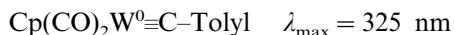
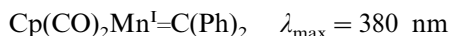
This photoreaction seems to be quite unique. The mechanism is unknown, but the radical pair Ti^0/Cp generated in the primary photochemical step apparently attacks the solvent in a subsequent reaction.

5. Metal-to-ligand charge transfer excited states

Owing to the highest energy of the Cp^- π^* -orbitals [2], MLCT transitions terminating at this ligand are not observed at low energies [2,5,8,9]. This notion is also consistent with the spectroscopic and photochemical properties of $\text{CpRe}^{\text{I}}(\text{CO})_3$ [6,28]. Rhenium(I) carbonyl complexes are well suited to detect low-energy MLCT transitions [6,29]. However, $\text{CpRe}(\text{CO})_3$ is characterized by a low-energy LF excited state, which is not emissive but photoreactive [6,28].

In complexes of the composition $\text{CpRe}(\text{CO})_2\text{L}'$ (L' = a series of pyridine derivatives) the ML'CT excited states are now located below the LF states [6,12,28]. Accordingly, these compounds show an emission, which originates from the lowest MLCT excited states. A variety of other $\text{Re}(\text{I})$ carbonyl complexes, which contain ligands with low-energy π^* -orbitals, are also characterized by emissive MLCT states [6,12,29,30].

Of course, a variety of other mixed-ligand Cp complexes, which contain a reducing metal ion and a suitable acceptor ligand, display MLCT absorptions at rather long wavelength. Particularly, carbene and carbyne complexes are appropriate examples [31,32]: e.g.

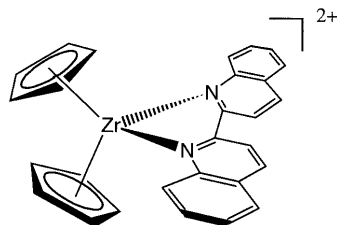


The MLCT states of these complexes are photoactive. Interestingly, the Main Group metal complex $[(\text{C}_5\text{Me}_5)\text{Sn}^{\text{II}}(\text{bipy})]^+$ also shows a MLCT ($\text{Sn}^{\text{II}} \rightarrow \text{bipy}$) absorption at rather long wavelength [18].

6. Ligand-to-ligand charge transfer excited states

LLCT transitions have attracted much attention in recent years. Electron donors are, for example, alkyl and aryl anions, while 1,2-diimines such as 2,2'-bipyridyl

function as electron acceptors [1,33–35]. Accordingly, complexes such as $\text{Zn}(\text{1,4-diaza-1,3-butadiene})\text{Et}_2$ ($\lambda_{\text{max}} = 490 \text{ nm}$) [36] are characterized by low-energy LLCT states. It follows that Cp^- should also serve as a donor for LLCT transitions. Recently, we explored this possibility and synthesized the cation $[\text{Cp}_2\text{Zr}^{\text{IV}}\text{biq}]^{2+}$ with $\text{biq} = 2,2'$ -biquinoline in order to identify such a LLCT state [37].



The design of this compound was guided by several considerations. $\text{Zr}(\text{IV})$ was chosen as the metal center because it has a d^0 electron configuration and is hardly oxidizing. Consequently, any interference with low-energy LF or LMCT transitions is avoided. Indeed, $[\text{Cp}_2\text{Zr}(\text{biq})]^{2+}$ shows a long-wavelength LLCT ($\text{Cp}^- \rightarrow \text{biq}$) absorption ($\lambda_{\text{max}} = 360 \text{ nm}$). Moreover, this LLCT state is also emissive ($\lambda_{\text{max}} = 518 \text{ nm}$, Fig. 3). In this context it is quite intriguing that $[\text{Cp}_2\text{Zr}(\text{biq})]^{2+}$ shares some features with the photosynthetic reaction center. The oblique pair of Cp^- ligands finds its counterpart in the chlorophyll special pair, while biq acts as electron acceptor in analogy to the quinone in the natural system. Of course, there are also important differences. In the photosynthetic reaction center an excited-state electron transfer takes place. On the contrary, in $[\text{Cp}_2\text{Zr}(\text{biq})]^{2+}$ a direct optical CT occurs since the donors and acceptor are coupled electronically by the intervening metal.

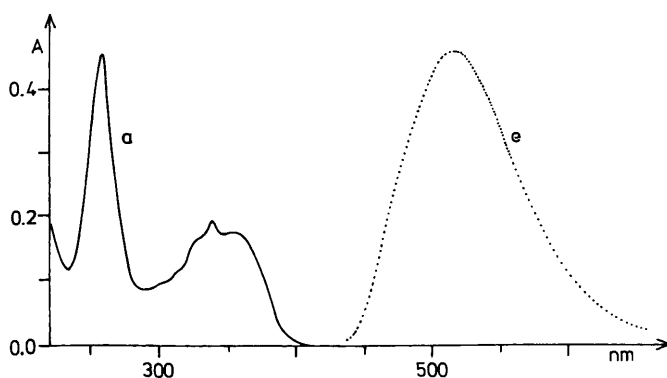
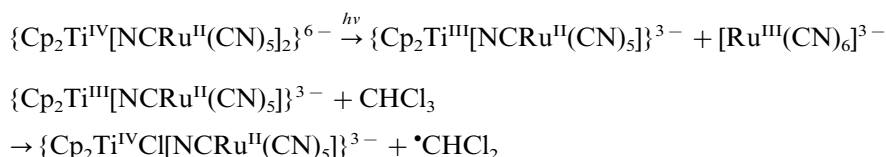


Fig. 3. Electronic absorption (a, —) and emission (e, ...) spectra of $2.18 \times 10^{-5} \text{ M}$ $[\text{Cp}_2\text{Zr}(\text{biq})]^{2+}$ at room temperature under argon in THF in a 1-cm cell. Emission: $\lambda_{\text{exc}} = 380 \text{ nm}$, intensity in arbitrary units.

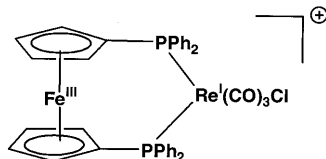
7. Metal-to-metal charge transfer excited states

The majority of bi- or polynuclear complexes, which simultaneously contain a reducing and an oxidizing metal, are of the mixed-valence (MV) type [5,38–40]. In their electronic spectra they show a long-wavelength MMCT (or intervalence, IT) absorption. Binuclear MV complexes, which are composed of a ferrocene and a ferrocenium cation, are well known to display a low-energy IT band [5,41]. The observation of MMCT absorptions is not restricted to MV compounds. Suitable heteronuclear complexes are also characterized by low-energy MMCT transitions [5,42,43]. We have recently synthesized such Cp complexes. For example, $\text{Cp}_2\text{Ti}^{\text{IV}}[\mu\text{-NCRu}^{\text{II}}(\text{CN})_5]_2^{6-}$ shows its MMCT ($\text{Ru}^{\text{II}} \rightarrow \text{Ti}^{\text{IV}}$) absorption at $\lambda_{\text{max}} = 630 \text{ nm}$ [44]. When Ti(IV) is replaced by the less oxidizing metals Zr(IV) and Hf(IV) the MMCT band is shifted to shorter wavelength at $\lambda_{\text{max}} = 420$ and 365 nm , respectively. The titanium complex undergoes a photoredox reaction upon MMCT excitation. In CHCl_3 the photolysis proceeds according to the scheme:



The titanium(III) intermediate is reoxidized by the solvent.

A rather intriguing binuclear complex contains ferrocenium as an acceptor and rhenium(I) as a donor [45]. Both metals are coupled by phosphine moieties:

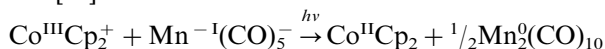


This ion displays a very broad MMCT ($\text{Re}^{\text{I}} \rightarrow \text{Fe}^{\text{III}}$) absorption at $\lambda_{\text{max}} = 700 \text{ nm}$. An analysis of this system leads to the conclusion that both metals interact only weakly. It is not clear if metal–metal coupling occurs through bonds or space. The complex is neither emissive nor photoactive.

8. Outer sphere charge transfer excited states

CT transitions may not only occur as intramolecular processes but may also occur between separate molecules or ions [46,47]. Intermolecular optical CT is also termed outer sphere charge transfer. Such OSCT transitions can be observed when a reducing and an oxidizing species are kept in close proximity in order to mediate an electronic interaction. A direct contact is achieved if electron donor and acceptor are oppositely charged and form ion pairs. This type of OSCT has been observed for a large number of coordination compounds including organometallics [46,47].

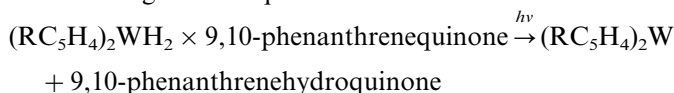
For example, the cobaltocenium cation is a suitable electron acceptor while metal carbonyl anions such as $\text{Co}(\text{CO})_4^-$ and $\text{Mn}(\text{CO})_5^-$ are appropriate electron donors. The ion pairs $\text{CoCp}_2^+ \text{Co}(\text{CO})_4^-$ [48] and $\text{CoCp}_2^+ \text{Mn}(\text{CO})_5^-$ [49] show OSCT absorptions at $\lambda_{\text{max}} = 520$ and 740 nm, respectively. Both salts are light sensitive. The general photochemical behavior of such ion pairs is illustrated by the following equation [49]:



OSCT excitation leads to the generation of cobaltocene and a $\text{Mn}(\text{CO})_5$ radical in the primary photochemical step. Product formation occurs by dimerization of the radical to yield the binuclear metal carbonyl.

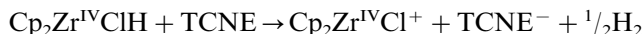
OSCT interactions may not only take place in ion pairs but also between neutral species [46]. It is well known that ferrocene and some of its derivatives form addition compounds with certain electron acceptors including trinitrobenzene and tetracyanoethylene (TCNE). These addition compounds are intensely colored owing to the presence of an OSCT ($\text{FeCp}_2 \rightarrow \text{acceptor}$) absorption in the visible spectral region [46,50].

The complex $\text{Cp}_2\text{M}^{\text{IV}}\text{H}_2$ ($\text{M} = \text{Mo}, \text{W}$) also forms colored adducts with a variety of electron accepting compounds such as olefins and aromatic molecules which carry electron-withdrawing substituents [51]. Recently, we examined the addition compound $(\text{RC}_5\text{H}_4)_2\text{WH}_2 \times 9,10\text{-phenanthrenequinone}$ ($\text{R} = i\text{-C}_3\text{H}_7$) [52]. It displays an OSCT absorption at $\lambda_{\text{max}} = 530$ nm. OSCT excitation is followed by H_2 transfer according to the equation:



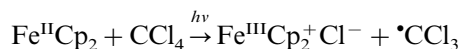
In this context it is quite interesting that Cp_2WH_2 is light sensitive itself and simply releases H_2 upon irradiation [6,7]. However, this photoreaction can apparently not be utilized for direct hydrogenations.

It has been suggested that the electron-donating property of Cp_2WH_2 in these addition compounds is based on the $\text{M}(\text{IV}) d^2$ metal ions [51]. As an alternative, the hydride ligands (or in other terms the M-H bonds) may provide the electron-donating site. We explored this possibility and studied the interaction between $\text{Cp}_2\text{Zr}^{\text{IV}}\text{ClH}$ and TCNE [53]. In this case only the Zr-H bond can donate electrons to TCNE and not $\text{Zr}(\text{IV})$ which is a d^0 metal ion. Unfortunately, an OSCT absorption was not observed because a facile thermal electron transfer took place:

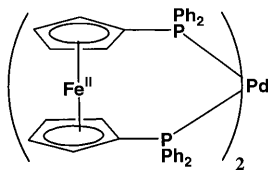


This result shows that M-H bonds could also act as donors in OSCT transitions.

A related type of intermolecular CT interaction takes place when certain electron-donating complexes are dissolved in electron-accepting solvents, in particular chlorinated alkanes such as CHCl_3 . As a result charge-transfer-to-solvent (CTTS) absorptions appear. It is well known that ferrocene in CCl_4 displays such a CTTS band in the near UV spectral region [6,54]. CTTS excitation leads to the photooxidation of ferrocene:



An intriguing variation of this photoredox process was observed recently. The trinuclear complex $\text{Pd}^0[(\text{PPh}_2\text{C}_5\text{H}_4)_2\text{Fe}^{\text{II}}]_2$ in CCl_4 shows a CTTS band at $\lambda_{\text{max}} = 338$ nm [55].



There is little doubt that this CTTS transition involves the ferrocene moiety as the donor site. CTTS excitation finally leads to the oxidation of $\text{Pd}(0)$ to $\text{Pd}(\text{II})$ yielding $\text{Pd}^{\text{II}}[(\text{PPh}_2\text{C}_5\text{H}_4)_2\text{Fe}^{\text{II}}]\text{Cl}_2$ as a stable photoproduct. It is suggested that the irradiation initially induces the generation of $\text{Fe}(\text{III})$ in analogy to ferrocene. In a subsequent thermal electron transfer $\text{Fe}(\text{III})$ oxidizes $\text{Pd}(0)$ to $\text{Pd}(\text{I})$, which undergoes a disproportionation to $\text{Pd}(0)$ and $\text{Pd}(\text{II})$. This photoredox reaction represents a novel type of photoinduced electron transfer in polynuclear complexes.

9. Conclusion

The electronic spectroscopy and photochemistry of cyclopentadienyl complexes reflects the amazing diversity encountered in coordination chemistry in general. While our basic knowledge on these compounds now stands on solid ground many applications are feasible and will be certainly developed in the near future.

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