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Photoreactivity of metal-to-ligand charge transfer excited states

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Contents

Abstract

Generally, transition metal complexes in metal-to-ligand charge transfer (MLCT) excited states are considered to be less reactive than in other states (e.g. ligand field, ligand-to-metal charge transfer) because the orbitals which participate in MLCT transitions are frequently of

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the π type and, thus, less involved in strong bonding interactions. However, contrary to these expectations, numerous complexes, in particular the organometallic compounds, are characterized by intrinsically reactive MLCT states. The photoreactivity may be correlated with the electron distribution in the excited state which roughly corresponds to an oxidized metal and reduced ligand when compared with the ground states. An attempt is made to classify reactive MLCT states according to the reactive center. The reactivity of a MLCT state may be based predominantly on the oxidation of the metal or reduction of the ligand. Finally, charge-transfer-to-solvent (CTTS) transitions which are closely related to MLCT transitions are included in this discussion.

Keywords: Charge transfer; Photochemistry; Transition metal complex

1. Introduction

Metal-to-ligand charge transfer (MLCT) excited states play an important role in the photophysics and photochemistry of transition metal complexes [1–6]. The overwhelming number of observations have been made on $d \rightarrow \pi^*$ MLCT states of polypyridyl complexes with reducing metals such as Ru^{II} [7,8] and Re^{I} [2,9]. In these cases, metal-to-ligand σ-bonding is not affected by CT excitation and structural rearrangements are small. Accordingly, such MLCT states are frequently not reactive, but strongly luminescent [2,7–10]. Of course, any molecule in any excited state including metal complexes in MLCT states may participate in intermolecular electron transfer processes. In contrast to these polypyridyl complexes there are numerous other coordination compounds which are characterized by intrinsically reactive and generally non-luminescent MLCT states.

In a simplified picture complexes in MLCT states can be described as species which contain oxidized metals and reduced ligands when compared with the electron distribution in the ground state. The excited state reactivity may then be attributed either to the properties of the oxidized metal center or the reduced ligand. Naturally, it is not always possible to separate both effects, but this approach should facilitate the comprehension of this subject. According to this distinction, the following cases will be discussed:

1. Reactivity of MLCT states based on the oxidation of the metal. Subsequent processes include associative ligand substitution, exciplex formation and cleavage of metal–metal bonds.
2. Reactivity of MLCT states based on the reduction of ligands. MLCT excitation may induce ligand isomerization and even dissociative ligand substitution when the ligands are involved in strong metal–ligand π-bonding. As another possibility the ligand undergoes a transformation induced by an electrophilic attack of a suitable substrate. Moreover, the ligand might be reduced irreversibly. Finally, ligand reduction can lead to an oxidative addition. MLCT states of the $d \rightarrow \pi^*$ as well as $d \rightarrow \sigma^*$ type may initiate such intramolecular redox reactions.
3. Charge-transfer-to-solvent (CTTS) excitation. CTTS transitions are closely related to MLCT and metal-centered Rydberg (or interconfigurational) transitions. These transitions could finally lead to an irreversible reduction of the

solvent leaving behind an oxidized complex. In suitable cases, stable products are generated by an oxidative addition of the solvent.

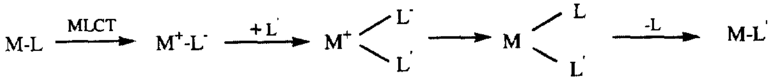
Generally, the identification of MLCT states is based on spectroscopic evidence which is usually facilitated if MLCT transitions occur at relatively low energies [11]. This requires the presence of reducing metals and oxidizing ligands or in spectroscopic terms ligands with empty orbitals at low energies. However, straightforward correlation between the nature of the excited state, directly reached by light absorption, and the observed photoreaction does not always exist and may be obscured by intervening excited states of different origin. Moreover, the extent of charge transfer achieved in a CT transition can differ considerably. It depends on the degree of delocalization of the orbitals involved in a CT transition. In extreme cases a charge shift may not occur at all. It follows that conclusions which are based on a charge transfer mechanism might not be valid.

Quite different classes of transition metal complexes have available low-energy MLCT excited states. However, the largest number of suitable complexes are organometallic compounds with metals in low oxidation states and π-accepting ligands. The present review deals with organometallics as well as other types of coordination compounds. Our report is not intended to treat this subject comprehensively, but rather to illustrate the diversity of reactive MLCT states by selected examples. Frequently, we have chosen our own work, but other studies are included as well.

2. Reactivity of MLCT states originating from the oxidized metal

2.1. Associative ligand substitution

MLCT transitions are associated with a shift of electron density from the metal to the ligand. In most cases, MLCT transitions take place between π-orbitals. The d^6 complexes $Ru(bipy)_3^{2+}$ [7,8] or $Re(bipy)(CO)_3Cl$ [2,10] are examples of this type. M–L σ-bonding is then not affected strongly by CT excitation. It should even strengthen M–L bonding by an increased electrostatic attraction between the oxidized metal and reduced ligand [2]. However, the increased positive charge at the metal is expected to facilitate reactions with nucleophiles. Since ligands are nucleophile by definition complexes in MLCT excited states may be susceptible to an associative ligand substitution:



$$M\text{-}L \xrightarrow{MLCT} M^{+}\text{-}L^{-} \xrightarrow{+L'} M^{+}\begin{smallmatrix} L^{-} \\ L' \end{smallmatrix} \longrightarrow M\begin{smallmatrix} L \\ L' \end{smallmatrix} \xrightarrow{-L} M\text{-}L'$$

However, this explanation is not always convincing. Let us consider octahedral d^6 complexes which assume a d^5 configuration in the MLCT state. Generally, d^5 complexes which can be also generated by chemical or electrochemical oxidation of the d^6 complexes are indeed less stable than their reduced counterparts, but usually undergo only relatively slow substitution reactions. Accordingly, it is not obvious that photosubstitutions of this type can originate from short-lived MLCT states. On the other hand, several cases of associative ligand substitution induced by MLCT excitation seem to be supported by experimental evidence and theoretical arguments. The following photoreactions are examples of substitutions which are assumed to proceed by an associative mechanism involving MLCT states [2,12–17]:

$$Co(CO)_3NO + PPh_3 \rightarrow Co(CO)_2(NO)(PPh_3) + CO,$$

$$W(CNR)_6 + py \rightarrow W(CNR)_5py + CNR,$$

$$W(CO)_4(\alpha - \text{diimine}) + PR_3 \rightarrow W(CO)_3(PR_3)(\alpha - \text{diimine}) + CO.$$

The tetrahedral complex $Co(CO)_3NO$ contains Co^{-I} with a d^{10} configuration and a NO^+ ligand. LF excited states are not available, but the complex does possess a low-energy $Co^I \rightarrow NO^+$ MLCT excited state. In a limiting description, the excited complex can be viewed as the redox isomer $Co^I(CO)_3(NO^-)$. Such a d^8 complex can easily adopt the coordination number five in analogy to $Fe(CO)_5$. Accordingly, $CO^I(CO)_3(NO^-)$ may accept a further ligand. Returning to the ground state, it is stabilized by the ejection of a CO ligand [9]. The photosubstitution of certain isocyanide complexes may proceed by a similar mechanism [2,13]. MLCT excitation of $W(CNR)_6$ ($\lambda_{max} = 446$ nm, R = Ph) leads to substitution of CNR by pyridine. The photolysis is less efficient if R is a bulkier ligand. Again, an associative substitution seems to be operative. Such a mechanism applies also to the photochemical substitution of $W(CO)_4$(α-diimine) complexes [14–16]. This assumption is supported by various observations. The quantum yields depend on the concentration and on the steric and electronic properties of the substituting PR_3 ligand. The pressure dependence of the quantum yield led to the same conclusion [17].

2.2. Exciplex formation [18]

Copper(I) polypyridyl complexes are characterized by a tetrahedral geometry and low-energy MLCT transitions [19,20]. LF transitions are not present owing to the d^{10} configuration at the metal. The luminescence from the MLCT state is quenched by various anions such as BPh_4^-, PF_6^-, BF_4^-, ClO_4^-, NO_3^- [21] and by coordinating solvents [22,23]. In the MLCT excited state the metal center can be regarded as a Cu^{2+} ion which should adopt a square-planar structure, but provides empty coordination sites for additional weakly bonded ligands [22,23]. Accordingly, in the MLCT excited state, Cu(I) polypyridyl complexes should be susceptible to further coordination. This association in the excited state (exciplex formation) [18] is apparently responsible for the luminescence quenching. In agreement with this assumption, this quenching can be reduced or prevented when sterically demanding polypyridyl ligands [24] such as 2,9-diphenyl-1,10-phenanthroline [22,23,25–27] are coordinated at Cu(I). However, the exciplex formation is a reversible process and does not yield a substituted complex.

2.3. Cleavage of metal–metal bonds

MLCT transitions of complexes with M–M single bonds may involve the removal of an electron from the M–M σ-bonding orbital. The concomitant weakening of the M–M bond could finally lead to the dissociation of the metal–metal bond. In the case of the compounds such as $(OC)_5Re\text{-}Re(CO)_3(\alpha\text{-diimine})$ and $Ph_3Sn\text{-}Re(CO)_3(\alpha\text{-diimine})$ it was suggested that the observed splitting of the Re–Re and Sn–Re bond, respectively, is indeed initiated by a σ^b (M–M) → diimine MLCT excitation [2,28–30]. However, Stufkens and his group have recently shown that this description is too simple. Several excited states are close in energy and various excited state processes must be considered in order to explain all observations [9,14].

The square-planar d^8 complex $Ir(CNMe)_4^+$ exists as an oligomer $[Ir(CNMe)_4^+]_n$ solution [31] in analogy to $Pt(CN)_4^{2-}$ which undergoes an association in concentrated aqueous solution [32,33]. MLCT excitation of $[Ir(CNMe)_4^+]_n$ leads to the dissociation of the oligomer into its mononuclear components [31]. However, this reaction cannot be rationalized by simple arguments since the lowest-energy MLCT transition leads to the depopulation of a M–M σ-antibonding orbital.

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

3.1. Ligand dissociation or dissociative substitution

In organometallic complexes with metals in low oxidation states, metal–ligand π-bonding contributes considerably to the stability of these compounds. Accordingly, weakening of M–L π-bonds could result in a dissociation or dissociative substitution. A considerable weakening should take place when MLCT excitation involves the promotion of a M–L π-bonding electron to a ligand π^* orbital which is strongly antibonding with regard to M–L π-interaction. This effect may be sufficient to induce the release or substitution of a π-acceptor ligand.

The photolysis of $Pt^0(PPh_3)_2C_2H_4$ is an example of a dissociation initiated by $d\pi^*$ MLCT excitation [34]:

$$Pt^0(PPh_3)_2C_2H_4 \rightarrow Pt^0(PPh_3)_2 + C_2H_4.$$

Owing to the d^{10} electron configuration of Pt^0, LF excited states do not exist. MLCT excitation of $Pt^0(PPh_3)_2C_2H_4$ is associated with the population of the π^* orbital of ethylene, which is also π-antibonding with respect to the $Pt^0\text{–}C_2H_4$ interaction. In the MLCT excited state, the complex is apparently not stable, but undergoes a release of ethylene. The $Pt(PPh_3)_2$ fragment is rather reactive and subject to secondary reactions such as HCl abstraction from $CHCl_3$ or intramolecular ortho-metallation.

In the fullerene complex $Pt^0[P(OPh)_3]_2C_{60}$ the bonding pattern is similar to that of $Pt^0(PPh_3)_2C_2H_4$ because the interaction of platinum with the fullerene is essentially restricted to two adjacent carbon atoms of C_{60} [35,36]. Since C_{60} is a powerful electron acceptor its platinum complex displays a MLCT absorption at rather long wavelength ($\lambda_{max} = 770$ nm) [37]. Upon MLCT excitation the fullerene is released in the primary photochemical step [37]:

$$Pt[P(OPh)_3]_2C_{60} \rightarrow Pt[P(OPh)_3]_2 + C_{60}.$$

In the absence of any scavenger the starting complex is regenerated. However, in the presence of suitable substrates the reactive fragment $Pt[P(OPh)_3]_2$ is intercepted and stable photoproducts are formed. If the photolysis is carried out in chloroform an irreversible product formation takes place. $CHCl_3$ can add oxidatively to Pt(0) yielding Pt(II) complexes. In inert solvents such as toluene, oxygen may scavenge Pt(0) with the formation of $Pt[P(OPh)_3]_2O_2$.

A case in question is the photoaquation of Zeise's salt [38]:

$$[PtCl_3(C_2H_4)]^- + H_2O \rightarrow [PtCl_3(H_2O)]^- + C_2H_4.$$

Initially, it was concluded that a reactive LF excited state of this planar d^8 complex induces the ejection of ethylene which takes place in addition to chloride aquation [38]. In a subsequent study it has been suggested on the basis of theoretical considerations that $Pt^{II} \rightarrow C_2H_4$ MLCT excitation induces the aquation of ethylene [39]. This conclusion is in line with the ideas outlined above. However, while in the case of Pt(0) LF states do not exist, Pt(II) complexes have available LF states at energies comparable to those of MLCT states. Since LF, as well as MLCT, states may be dissociative, an unambiguous identification of the reactive excited state is more difficult to establish and has not yet been achieved.

$Ni(CO)_4$ also undergoes a photodissociation [40]:

$$Ni(CO)_4 \rightarrow Ni(CO)_3 + CO.$$

In the presence of a potential ligand, a substitution takes place [41]. The photoreactivity of $Ni(CO)_4$ was attributed to a metal-centered 3d → 4s [2] or MLCT excited state [42], since LF states are not available. Later calculations suggest that ds states can be excluded as reactive states because they occur at too high energies [43].

Complexes of the type $Ni(CO)_2(DAB)$ with DAB = 1,4-diazabutadien (RN = CH–CH=NR) are further examples of dissociative MLCT states [14,44]. The tetrahedral complex $Ni(CO)_2$(*t*-Bu-DAB) shows a low-energy $Ni^0 \rightarrow$ DAB MLCT band around 500 nm [14,45]. Upon MLCT excitation, a Ni–N bond is broken in the primary photochemical step. Depending on the reaction conditions, various products are formed in secondary reactions. In the case of $Ni(CO)_2$(*i*-Pr_2-Ph-DAB) it was shown by resonance Raman spectroscopy that the MLCT state is also strongly π antibonding with regard to the Ni–CO interaction. Consequently, MLCT excitation is associated with the release of CO. In the presence of phosphines, complexes of the formula $Ni(CO)(PR_3)(DAB)$ are finally formed.

A detailed study of $Cr(CO)_4$(bipy) including time resolved absorption spectra has shown that MLCT excitation is also followed by a dissociative loss of CO [46]. However, a rather complicated mechanism was derived to account for all observations.

3.2. Irreversible ligand reduction

Generally, ligands are electron rich and not easily reduced to stable species. However, there are exceptions. Some ligands can undergo an irreversible decay upon reduction. Suitable candidates are nitrate and aryl diazonium cations:

$$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O,$$

$$R - C_6H_4 - N_2^+ + e^- \rightarrow R - C_6H_4^{\cdot} + N_2.$$

It follows that MLCT excitation terminating at these ligands should lead to the oxidation of the metal and reduction of the ligand. A reaction of this type has been observed upon irradiation of $Cu^I(PPh_3)_2NO_3$ [47]. This complex is characterized by an intraligand (IL) absorption of the phosphine in the UV. It is suggested that IL excitation is followed by the population of a reactive $Cu^I \rightarrow NO_3^-$ MLCT state. The electron is accepted into the π^* orbital of nitrate which is then reduced to NO_2:

$$Cu^I(PPh_3)_2NO_3 \rightarrow Cu^{II}(PPh_3)_2O + NO_2.$$

This primary photochemical step is followed by subsequent reactions including the oxidation of PPh_3 by NO_2. Cu(II), Ph_3PO and NO are final products of this photolysis.

Arene diazonium cations are well known as ligands. Since these cations are electron acceptors, complexes with reducing metals should display low-energy MLCT absorptions. Unfortunately, the electronic spectra and photochemistry of complexes with arene diazonium complexes have not yet been studied. However, the feasibility of a photoredox reaction of the $M\text{-}N_2C_6H_4R$ moiety induced by MLCT excitation is demonstrated by a related outer sphere CT process (J. Kisslinger and A. Vogler, unpublished results) [48]:

$$CH_3O - C_6H_4 - N_2^+/[Ru^{II}(CN)_6]^{4-} \xrightarrow{h\nu} CH_3O - C_6H_4 - N_2 + [Ru^{III}(CN)_6]^{3-},$$

$$CH_3O - C_6H_4 - N_2^{\cdot} \rightarrow CH_3O - C_6H_4^{\cdot} + N_2.$$

The ion pair between the diazonium cation and $[Ru(CN)_6]^{4-}$ shows a $Ru^{II} \rightarrow CH_3O\text{-}C_6H_4\text{-}N_2^+$ CT absorption at $\lambda_{max} = 375$ nm. Upon light absorption by this CT band, the diazonium cation is reduced irreversibly, while $[Ru(CN)_6]^{4-}$ is oxidized to $[Ru(CN)_6]^{3-}$ with $\phi = 0.02$ at $\lambda_{irr} = 405$ nm.

3.3. Ligand isomerization

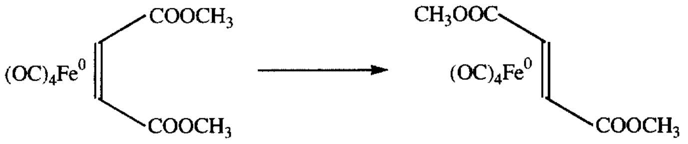
A ligand which is reduced in a MLCT state may undergo an isomerization reaction. Subsequent back electron transfer yields the complex with the isomerized ligand. For example, a MLCT transition which terminates at the π^* orbital of an olefin ligand leads to a weakening of the double bond of the olefin. As a result, the olefin could undergo a *trans/cis* photoisomerization. This behavior is shown by Ru(II) complexes with *trans/cis*-4-styryl-pyridine ligands which are coordinated via nitrogen atoms. The cations $[Ru(bipy)_2(4\text{-styryl-pyridine})_2]^{2+}$ and $[RuCl(bipy)_2(4\text{-styryl-pyridine})]^+$ show $Ru^{II} \rightarrow$ styryl-pyridine MLCT absorptions between 350 and

500 nm [49]. In the MLCT excited state the ligand undergoes apparently a rotation around the central C–C bond [49]:

$$[\mathrm{Ru(bipy)_2}(cis-4-\text{styryl}-\text{pyridine})_2]^{2+}$$
$$\rightarrow[\mathrm{Ru(bipy)_2}(trans-4-\text{styryl}-\text{pyridine})_2]^{2+}.$$

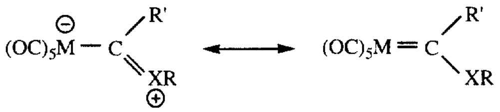
Both styryl-pyridine ligands react independently. The quantum yield of this photoisomerization is $\phi=0.51$ at $\lambda_{\mathrm{max}}=436$ nm. In addition to this MLCT-induced photolysis, the *trans/cis* isomerization of the coordinated styryl-pyridine takes also place upon IL excitation at shorter wavelength.

In distinction to these styryl-pyridine complexes, olefins may be also coordinated side on. It has been pointed out earlier that π-backbonding is important in these complexes. Accordingly, MLCT transitions terminating at the π^* (olefin) orbitals may lead to release of the olefin. As an alternative, the olefin can participate in a *trans/cis* isomerization in analogy to the styryl-pyridine complexes. In some cases, such a photoisomerization of side-on coordinated olefins has been observed. Although the nature of the reactive excited state is not always clear, there are indications that these reactions are indeed induced by metal → π^* (olefin) MLCT transitions. For example, MLCT excitation of $\mathrm{Fe(CO)_4}$(oelfin) complexes yields the isomerized ligand [42,50]:



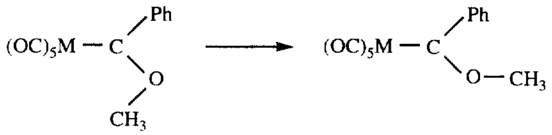
However, this photoconversion of methylmaleate to dimethylfumarate is accompanied by substitution reactions which seem to be initiated by LF excitation.

Another type of ligand photoisomerization takes place upon MLCT excitation of the carbene complexes $\mathrm{M(CO)_5C(XR)R'}$ with M = Cr, W and X = 0, NH [51]. Their electronic ground state structures are represented by two resonance forms:



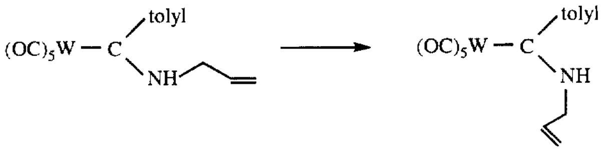
I II

The partial double band character of the C–X bond in the carbene ligand is associated with the existence of stereoisomers. The MLCT transition to the π^* orbital of the coordinated carbene leads to the prevalence of resonance form II which allows free rotation around the C–X bond. MLCT excitation induces then an *anti* to *syn* isomerization [51]:



This photolysis was observed in low-temperature matrices. The assumption of a reactive MLCT state was confirmed by resonance Raman spectroscopy.

In the case of X = NH the *E*-isomer is photoconverted to the *Z*-form [52–54]:

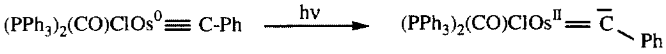


While this isomerization is apparently initiated by W → carbene MLCT excitation, a concomitant CO loss seems to originate from LF excited states.

3.4. Ligand transformations induced by electrophilic attack at the reduced ligand

As described above Co^{-I}(CO)$_3$(NO$^+$) in its MLCT excited state can be viewed as a Co(I) complex which contains a NO$^-$ ligand. While in solution the complex undergoes a light-induced associative substitution, the photolysis takes a different course in the gas phase [12]. The coordinated NO$^-$ ligand is susceptible to a electrophilic attack by H$^+$ which originates from HCl. This reaction generates HNO which decomposes to water and N_2O. The photolysis of Co(CO)$_3$(NO) and HCl in the gas phase yields finally $CoCl_2$, N_2O, H_2O and CO.

The photoreactions of certain carbyne complexes are related to that of CO(CO)$_3$(NO). MLCT excitation is associated with a shift of electron density from the metal to the carbyne ligand. In a limiting description, a two-electron transfer takes place [55]:

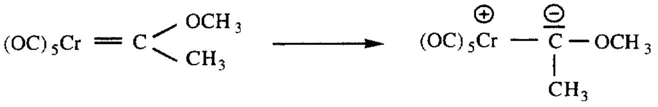


$$(PPh_3)_2(CO)ClOs^0\equiv C\text{-}Ph \xrightarrow{h\nu} (PPh_3)_2(CO)ClOs^{II}=\bar{C}\diagdown_{Ph}$$

In the presence of HCl, the coordinated carbene anion is protonated to a carbene and chloride adds to Os(II) to complete the octahedral coordination of the d^6 metal center. The resulting carbene complex Os^{II}(CHPh)(PPh$_3$)$_2$(CO)Cl$_2$ is formed with $\phi = 0.1$ at $\lambda_{irr} = 365$ nm. An analogous reaction occurs upon MLCT excitation of [Os^0(CPh)(PPh$_3$)$_2$(CO)$_2$]$^+$ [55].

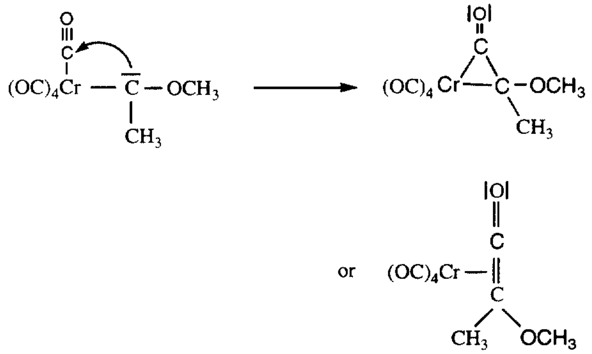
More complicated transformations of carbyne ligands are also attributed to reactive MLCT states [3,54]. However, the participation of other coordinated ligands such as CO may indicate an interference by reactive LF excited states.

Some aspects of the photoreactivity of carbene complexes induced by MLCT excitation have been discussed in the preceding sections. Other photoreactions can be also attributed to MLCT excited states. MLCT excitation could finally lead to an intermediate which carries a lone pair at the coordinating carbon atom:



$$(OC)_5Cr=C\begin{matrix}\nearrow OCH_3\\ \searrow CH_3\end{matrix} \longrightarrow \overset{\oplus}{(OC)_5Cr}-\overset{\ominus}{\underset{\displaystyle CH_3}{\underset{|}{\bar{C}}}}-OCH_3$$

Since carbonyl ligands are electrophiles they may react in an intramolecular process with the reduced carbene ligand [3,56]:



These processes are apparently reversible. However, in the presence of suitable substrates such as imines the coordinated ketene undergoes addition reactions which can be utilized for the synthesis of a variety of organic compounds [3,56].

3.5. *Ligand reduction resulting in oxidative addition*

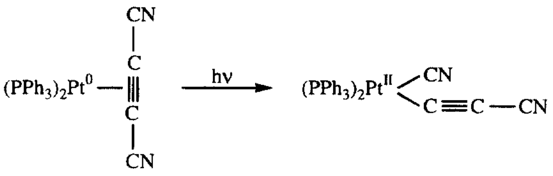
Oxidative additions take place by a reductive cleavage of a σ-bond. Two electrons are transferred from a metal to some substrate which yields two anions. Subsequently, these anions are added as ligands to the oxidized metal:

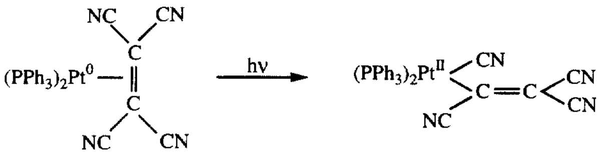
$$M^{n+} + A - A' \rightarrow A - M^{n+2} - A'.$$

If A–A′ can serve as a ligand for M^{n+} the oxidative addition occurs as an intramolecular process. It is quite obvious that such reactions should be promoted or facilitated by MLCT excitation within the M^{n+}–AA′ moiety. Intramolecular oxidative additions are induced by MLCT transitions which terminate at π^* or σ^* orbitals of A–A′.

3.5.1. *π^*-acceptors*

The following photochemical oxidative additions illustrate this type of reaction [57,58]:





Nitrile-substituted acetylene (DCNA) and ethylene (TCNE) are powerful acceptors. Since Pt^0 is reducing the lowest-energy transitions of $Pt(PPh_3)_2(DCNA)$ and $Pt(PPh_3)_2(TCNE)$, it should involve $Pt^0 \rightarrow \pi^*$ (DCNA or TCNE) MLCT. Finally, MLCT excitation is followed by oxidative additions. In the case of TCNE complex, the intermediate formation of the one-electron reduced ligand (TCNE radical anion) was observed [58]. Of course, the MLCT transition is not directly related to product formation because it leads to the population of a π^* orbital of the ligand while the oxidative addition requires the reductive splitting of a C–C σ-bond within the ligand. It follows that the primary product must undergo a considerable rearrangement in order to result in an oxidative addition.

A similar oxidative addition was also suggested to be induced by MLCT excitation. Irradiation of either (*cis*-$CHBr{=}CHBr)Fe(CO)_4$ or (*trans*-$CHBr{=}CHBr)Fe(CO)_4$ led to an intramolecular insertion of iron into one of the carbon–bromine bonds of the coordinated olefin to yield $(CO)_4BrFe{-}CH{=}CHBr$ as primary photoproduct [42,50]. Since the iron was shown to be *trans* to the bromine of the σ-bonding $-CH{=}CHBr$ ligand, a rotation about the olefinic double bond must have occured in the case of (*cis*-$CHBr{=}CHBr)Fe(CO)_4$ as starting complex. It was concluded that these insertion reactions originate from $d \rightarrow \pi^*$ (olefin) CT transitions; they were assigned to the lowest energy absorptions in the electronic spectra of (*cis*- and *trans*-$CHBr{=}CHBr)Fe(CO)_4$. Since the π^* level of $CHBr{=}CHBr$ is antibonding for both the C–C and C–Br bonds as well, the CT excited state was assumed to facilitate free rotation about the olefinic bond and insertion of the positively charged iron into a C–Br bond by a nucleophilic attack of the olefinic radical anion.

3.5.2. σ^*-*acceptors*

MLCT transitions which terminate at the σ^* orbitals of ligands are directly related to oxidative additions since the reductive cleavage of a σ-bond requires the population of the corresponding σ^* orbital. Unfortunately, σ^* orbitals occur generally at rather high energies and are, thus, not available for low-energy electronic transitions. However, some oxidizing molecules, such as I_2 and Se_2Ph_2, or ions (e.g. O_2^{2-}) are exceptions and provide low-energy σ^* orbitals. Accordingly, MLCT transitions at reasonable energies should be observed if these species are coordinated to reducing metals. A few complexes of this type are known and have been studied quite recently with regard to their electronic spectra and photochemistry.

The binuclear ligand-bridged complex $Re_2^IBr_2(CO)_6(Se_2Ph_2)$ show a long-wavelength absorption at $\lambda_{max} = 434$ nm which is assigned to the $Re^I \rightarrow \sigma^*(Se_2Ph_2)$ MLCT transition [59]. Upon MLCT excitation the compound decomposes. It is suggested that the primary photochemical step is an oxidative addition [59]:

$$Re_2^I(Se_2Ph_2) \rightarrow 2Re^{II}(SePh).$$

In distinction to mononuclear complexes, two metal centers are involved in this case.

The complex $Cr(O_2)_2(NH_3)_3$ contains Cr(IV) and two peroxide ligands which are bonded side on. This compound displays an absorption at $\lambda_{max} = 390$ nm which is attributed to a MLCT transition terminating at the σ^* orbital of peroxide [60]. MLCT oxidation leads to a clean intramolecular oxidative addition:

$$Cr^{IV}(O_2)_2(NH_3)_3 + 2H_2O \rightarrow (NH_4)_2[Cr^{VI}O_4] + H_2O_2 + NH_3.$$

The photolysis can be driven to completion. Chromate is formed with $\phi = 0.35$ at $\lambda_{max} = 254$ nm [60].

4. Charge transfer to solvent (CTTS) excitation

Numerous photoreactions of transition metal complexes are associated with the oxidation of the metal and donation of the metal electron to the solvent [1–6]. Solvated electrons are detected by ESR or visible spectroscopy. They give rise to a long-wavelength absorption which is responsible for the blue color of such solutions. Generally, they are stable only in certain solvents (e.g. liquid ammonia) or low-temperature matrices, but appear as transients in most solvents at room temperature, for example in water with $\lambda_{max} = 720$ nm, $\epsilon = 18500$. These solvated electrons may finally undergo recombination with the oxidized complex, reduce the solvent or any other suitable substrate present in the solution.

Usually, it is assumed that solvated electrons are generated by CTTS transitions which cause a characteristic absorption in the electronic spectrum [1–6]. CTTS is a special type of outer sphere charge transfer which is observed for a variety of different systems including ion pairs which consist of oxidizing cations and reducing anions [48]. However, CTTS bands are often difficult to identify owing to their interference with other absorptions. Unspecified solvent shifts can obscure the electronic spectrum and complicate band assignments. At this point, it should be emphasized that CTTS transitions are closely related to MLCT transitions, since their acceptor orbitals (e.g. π^* of cyanide) are exposed to the solvent. Accordingly, an outer-sphere interaction with the solvent can take place. A CTTS transition may, thus, be just a special type of MLCT transition. In this context, it is quite interesting that the common properties of MLCT and CTTS transitions will be also observed for other electronic transitions which involve the promotion of a metal electron to any orbital exposed to the solvent. For example, metal-centered Rydberg (or interconfigurational) transitions lead to the excitation of a metal electron to an orbital of the next higher quantum number (e.g. $3d \rightarrow 4s$ at Cu^+). Since the acceptor orbital has a large extension and is rather diffuse, the electron in such an orbital has a considerable probability to reside at a ligand [61] or solvent shell [62]. It follows from these considerations that MLCT, CTTS and interconfigurational transitions are interrelated and able to initiate the formation of solvated electrons.

Generally, the photactive complexes contain reducing metals which facilitate their photooxidation and concomitant formation of solvated electrons. The majority of studies have been performed with d^6 and d^{10} metals, but others including d^8 metals are also known to undergo the photogeneration of solvated electrons.

4.1. d^6 complexes

The electronic spectrum of $[Fe(CN)_6]^{4-}$ shows a long-wavelength LF band at $\lambda_{max} = 320$ nm and shorter-wavelength absorptions which were assigned to MCLT [63] and CTTS transitions [64]. Aqueous $[Fe(CN)_6]^{4-}$ represents the prototype of complexes which generate solvated electrons upon CT excitation [65–69]:

$$[Fe^{II}(CN)_6]^{4-} \rightarrow [Fe^{III}(CN)_6]^{3-} + e_{aq}^{-}.$$

These solvated electrons are stable in low-temperature (77 K) glasses of concentrated NaOH solution. The presence of electrons is indicated by a blue coloration at longer irradiation times. In aqueous solution at room temperature, these solvated electrons appear as transients. They can be scavenged by N_2O. Other reducing cyano complexes such as $[Ru(CN)_6]^{4-}$, $[Mo(CN)_8]^{4-}$ and $[W(CN)_8]^{4-}$ show an analogous behavior [65–69]. The molybdenum and tungsten complexes contain d^2 metal ions.

The photolysis of aqueous Fe^{2+} is also associated with the formation of solvated electrons [70,71] and leads finally to the reduction of water [4,72,73]:

$$Fe^{2+} + H_2O \rightarrow Fe^{3+} + 1/2H_2 + OH^-.$$

The photoactive electronic transition seems to be a direct photodetachment of electrons, but a 3d → 4s interconfigurational transition may be also photoactive [73]. The photolysis of aqueous Eu^{2+} leads also to the production of H_2 and photooxidation of the metal [74]. In the case of the f^7 ion Eu^{2+}, the photoactive electronic transition 4f → 5d is also of the Rydberg type.

Distinct CTTS absorptions appear in the electronic spectra of certain organometallic complexes in halocarbon solvents [2,75]. For example, ferrocene shows a new absorption at $\lambda_{max} = 307$ nm if it is dissolved in CCl_4 [76,77]. This band is assigned to a CTTS transition. Upon CTTS excitation, ferrocene is photooxidized [78,76]. The primary photochemical step proceeds according to the equation:

$$Fe^{II}(C_5H_5)_2 + CCl_4 \rightarrow Fe^{III}(C_5H_5)_2 + Cl^- + {}^{\bullet}CCl_3.$$

Owing to the irreversible reduction of CCl_4 ferrocenium ions are found as final photoproducts although secondary reactions lead to a further degradation. Solvated electrons are not observed during the photolysis of ferrocene in halocarbon solvents. It is suggested that the CTTS transition terminates directly in the σ^* orbitals of C–X bonds. These σ^* orbitals are located at relatively low energies [79].

This type of photooxidation was also observed for $[Ru(CN)_6]^{4-}$

$$[Ru^{II}(CN)_6]^{4-} + CHCl_3 \rightarrow [Ru^{III}(CN)_6]^{3-} + Cl^- + {}^{\bullet}CHCl_2.$$

This photolysis is very efficient ($\phi = 0.49$ at $\lambda_{irr} = 282$ nm) and can be used for the synthesis of $[Ru^{III}(CN)_6]^{3-}$ [77]. In contrast to ferrocene, CTTS bands were not detected in the electronic spectrum of $[Ru(CN)_6]^{4-}$ in $CHCl_3$, However, it is feasible that CTTS absorptions are present, but obscured by MLCT bands which appear in the same spectral region.

A variety of other transition metal complexes are also photooxidized in halocarbon solvents [2,6,76,80]. In most cases, an unambiguous identification of the reactive excited states has not yet been achieved. It is also possible that an excited state electron transfer mechanism applies to some of these photooxidations.

4.2. d^{10} complexes

Simple complexes of d^{10} metal centers have available only interconfigurational ds (and possibly dp) and MLCT excited states at accessible energies. The similarity of interconfigurational, MLCT and CTTS transitions with regard to photooxidations of metal complexes has been noted above. Accordingly, complexes of reducing d^{10} ions are excellent candidates for the observation of photooxidations.

A variety of Cu(I) complexes including $CuCl_3^{2-}$, $Cu(CN)_3^{2-}$ and $Cu(NH_3)_3^+$ are photooxidized in aqueous solution [4,20]. Aquated electrons were detected by flash photolysis. An irreversible product formation takes place if the electrons are intercepted by suitable scavengers such as N_2O, NO_3^-, NH_4^+ and H^+. In acidic solution or in the presence of ammonium ions the generation of H_2 was observed. The photoreduction of H^+ to H_2 is certainly of interest with regard to applications in solar energy conversion and storage. Unfortunately, simple Cu(I) complexes are colorless. Their photosensitivity is, thus, restricted to UV light.

The anion $[Fe(CO)_4]^{2-}$ which is isoelectronic with $Ni(CO)_4$ is stable in deaerated alkaline solutions. It absorbs only below 400 nm [81]. The spectrum is rather featureless and may consist of ds, MLCT and CTTS absorptions. Upon irradiation of $[Fe(CO)_4]^{2-}$ in glasses of aqueous NaOH at 77 K, the production of solvated electrons was observed [82]. The concomitant blue coloration of the matrix is caused by a broad absorption $\lambda_{max} = 588$ nm. The quantum yield of electron production is relatively low ($\phi = 0.03$ at $\lambda_{max} = 254$ nm).

Complexes of the type $[AuX_2]^-$ with $X = Cl$ and Br are characterized by long-wavelength ds absorptions [83,82]. In solutions of CH_2Cl_2 these complexes undergo a photooxidation to Au(III) [84]. For example, $AuCl_2^-$ is photooxidized to $AuCl_4^-$ with $\phi = 0.07$ at $\lambda_{max} = 254$ nm. It is assumed that $5d \rightarrow 6s$ excitation leads directly to the irreversible reduction of the solvent.

5. Conclusion

A large variety of transition metal complexes which consist of reducing metal centers and π-acceptor ligands are characterized by reactive MLCT excited states. In a simple approach, the photoreactivity can be related to the electron distribution in the CT state. Accordingly, the formation of photoproducts are attributed to the properties of the oxidized metal and/or reduced ligand. Interconfigurational (e.g. ds) and CTTS transitions share some common features with MLCT transitions. Photooxidations of metal complexes induced by CTTS and ds excitations are accompanied by the formation of solvated electrons or the reduction of the solvent.

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