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Excited state properties of organometallic compounds of rhenium in high and low oxidation states

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Abstract

Organometallic compounds of rhenium occur in high and low oxidation states. These complexes are characterized by a variety of excited states including ligand field (LF), ligand-to-metal charge transfer (LMCT), metal-to-ligand charge transfer (MLCT), ligand-to-ligand charge transfer (LLCT), metal-to-metal charge transfer (MMCT), and intraligand (IL) excited states. The nature of the lowest-energy excited state can be tuned by the choice of appropriate ligands and metal oxidation states. This diversity is illustrated by selected examples of organometallics of Re(VII) and Re(I). Our account emphasizes spectral (absorption and emission) as well as photochemical properties.

Keywords: Rhenium(VII); Rhenium(I); Absorption spectra; Emission spectra; Photochemistry; Organometallics

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1. Introduction

The photochemistry of organometallic compounds represents an important branch of coordination chemistry. The interest in this research field is based on fundamental aspects as well as applications. For a long time organometallic photochemistry has been restricted almost exclusively to compounds with transition metals in low oxidation states [1,2] while recently the significance of metals in high oxidation states has also been recognized. Usually, this diversity is demonstrated by compounds of quite different metals. However, rhenium is rather unique to form photoactive organometallic complexes over a wide range of oxidation states extending from 0 (e.g. $Re_2(CO)_{10}$) to VII (e.g. CH_3ReO_3).

While a classification according to the metal, its position in the periodic table or its d^n electron configuration is quite useful other categories are even more beneficial in the field of photochemistry. The comprehension of interrelations is facilitated when photoactive metal complexes are treated according to the nature of the reactive excited state because a certain type of electronic transition leads to similar consequences irrespective of the specific compound. Photochemical reactions may thus be attributed to the following excited states:

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

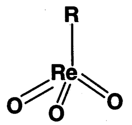
In particular, Re(VII) and Re(I) with their d^0 and d^6 electron configurations, respectively, are well suited to illustrate the versatility of excited state properties of organometallic compounds. The present review is an account for our own work in this area. However, some relevant observations of other groups are included in order to discuss this subject in a broader context.

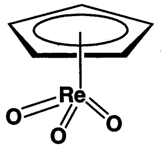
2. Rhenium(VII) compounds

In recent years the chemistry of organometallics with metals in high oxidation states has gained increased attention [3,4]. This interest, particularly in organometallic oxides [5,6], is related to the idea that such compounds might serve as molecular models for heterogeneous catalysis at metal oxide surfaces. In this context it is remarkable that metal oxides or solid oxometalates with d^0 metals in high oxidation states (e.g. V_2O_5, MoO_4^{2-}) have been shown to be promising photocatalysts for the transformation of organic compounds [7]. Similarly, polyoxometalates were found to selectively photoactivate C – H bonds [8]. It follows from these considerations that the study of the photochemistry of simple organometallic oxides should be of general importance. For this purpose we used organorhenium(VII) oxides [9–12] as attractive candidates. Simple compounds of this type are derived from perrhenate. One oxide ligand of ReO_4^- is replaced by a carbanion R^-. The parent compound CH_3ReO_3 has the ability to easily expand its coordination sphere. As a consequence the CT properties and photoreactivity of CH_3ReO_3 can be tuned by the addition of suitable ligands and generation of complexes of the general formula $CH_3ReO_3 \cdot L$. Of course, MC and MLCT transitions are not available owing to the empty valence shell of Re(VII).

2.1. Ligand-to-metal charge transfer (LMCT)

A variety of complexes with the general composition $RReO_3$ have been synthesized and characterized [9–12], e.g.:





R = CH_3, C_2H_5, $C_6H_2(CH_3)_3$

= C_5H_5, $C_5H_4CH_3$, $C_5(CH_3)_5$

Since these organorhenium(VII) oxides contain a d^0 metal center all electronic transitions are of the LMCT type. According to the reducing character of R^- the lowest-energy LMCT transitions involve the promotion of an electron from the carbanion to Re(VII) (Table 1) [13,14]. The acceptor orbital is π-antibonding with regard to the Re–O interaction as indicated by the vibrational progression of the LMCT absorption of CH_3ReO_3 [13].

The compounds $RReO_3$ are light sensitive [13,14]. Upon irradiation the complexes undergo a homolytic cleavage of the R–Re bond in agreement with the LMCT character of the lowest-energy excited states. However, the fate of the radical pair $R^{\bullet}/{}^{\bullet}ReO_3$ depends on the nature of R and the medium. If the radical $R^{\bullet}$ is relatively stable and less reactive a recombination to the starting complex is facilitated. Product formation becomes more efficient with increasing reactivity of

Table 1
LMCT absorptions and photochemical quantum yields of $RReO_3$ complexes

R	λ_{max} (nm)	ϕ (λ_{irr}/nm)
CH_3	260	0.58 (254)
C_2H_5	262	0.53 (254)
$C_6H_2(CH_3)_3$	334	0.18 (333)
C_5H_5	377	0.028 (313)
$C_5H_4CH_3$	380	0.013 (313)
$C_5(CH_3)_5$	402	0.0001 (313)

$R^\bullet$ since other reactions of $R^\bullet$ compete successfully with recombination. Accordingly, the quantum yield of product formation decreases in the order $CH_3 > C_2H_5 >$ mesityl $> C_5H_5 > C_5H_4(CH_3) > C_5(CH_3)_5$ (Table 1) in agreement with the increasing stability of the radical $R^\bullet$.

Several secondary steps including radical coupling ($2^\bullet R \rightarrow R_2$) contribute to product formation. However, the most important process involves hydrogen abstraction from a suitable substrate, in particular from the solvent. In aqueous solution the photolysis of CH_3ReO_3 proceeds essentially according to the equation:

$$CH_3ReO_3 + H_2O \rightarrow CH_4 + H^+ReO_4^-$$

Since methyl radicals are not able to abstract hydrogen atoms from bulk water it is assumed that $CH_3^\bullet$ attacks coordinated water. The reaction sequence can be described by the following scheme:

$$CH_3 - Re^{VII}O_3 + H_2O \rightarrow CH_3 - Re^{VII}(H_2O)O_3$$

$$CH_3^- Re^{VII}(H_2O)O_3 \xrightarrow{hv} CH_3^\bullet/^\bullet Re^{VI}(H_2O)O_3$$

$$CH_3^\bullet/^\bullet Re^{VI}(H_2O)O_3 \rightarrow CH_4 + H^+Re^{VII}O_4^-$$

In non-aqueous solutions the radicals $R^\bullet$ abstract hydrogen from the solvent and other sources or undergo dimerization while ReO_3 fragments aggregate to bulk rhenium trioxide.

CH_3ReO_3 provides free space for additional ligands [15]. The resulting complexes $CH_3ReO_3 \cdot L$ are not very stable, but dissociate in solution partly into CH_3ReO_3 and L. With regard to photochemistry these addition complexes provide ready access to other CT excited states. Upon addition of $Bu_4N(SH)$ to CH_3ReO_3 in methylene chloride the colorless solution turns violet owing to the appearance of a new absorption at $\lambda_{max} = 540$ nm (Fig. 1). Unfortunately, this species have not been identified since it is rather unstable as indicated by a rapid disappearance of the violet color. However, it is reasonable to assume that the formation of $MeReO_3 \cdot SH^-$ causes the violet coloration. The absorption maximum at $\lambda = 540$ nm is assigned to a $SH^- \rightarrow Re^{VII}$ LMCT transition in analogy to $Re^{VII}S_4^-$ ($\lambda_{max} = 505$ nm) [16].

CH_3ReO_3 reacts with H_2O_2 to generate $CH_3ReO_2(O_2)$ and $CH_3ReO(O_2)(H_2O)$ [17]. These compounds are efficient oxygen transfer catalysts. The latter complex

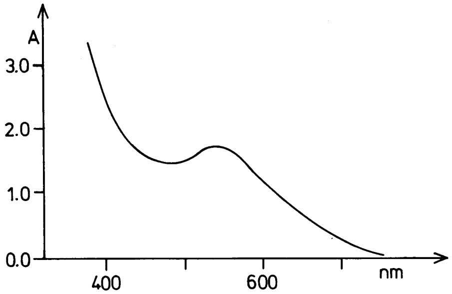


Fig. 1. Absorption spectrum of an equimolar mixture (2.1×10^{-3} M) of CH_3ReO_3 and $Bu_4N(HS)$ in methylenechloride at r.t., 1-cm cell.

shows a peroxide → Re^{VII} LMCT absorption at $\lambda_{max} \sim 360$ nm. LMCT excitation leads to a homolytic splitting of a rhenium–peroxide bond in the primary photochemical step. Finally, several photoproducts are formed [17].

2.2. Ligand-to-ligand charge transfer (LLCT)

The yellow color of the adduct CH_3ReO_3·bipy is associated with an absorption maximum at $\lambda = 360$ nm. It is assigned to a $CH_3^- \rightarrow$ bipy LLCT transition [18]. Such LLCT transitions from carbanion ligands to π* orbitals of suitable acceptor ligands have been identified for a variety of other organometallic compounds with metals in lower oxidation states [19–22]. The photolysis of aqueous CH_3ReO_3·bipy proceeds according to the following stoichiometry:

$$CH_3ReO_3\cdot\text{bipy} + H_2O \rightarrow CH_4 + \text{bipyH}^+ \ ReO_4^-$$

While this photoreaction leads essentially to the same product as that of aqueous CH_3ReO_3 it can be affected with longer-wavelength light ($\lambda_{irr} = 405$ nm) compared to CH_3ReO_3 ($\lambda_{irr} < 300$ nm). Accordingly, the bipy adduct acts as a long-wavelength sensitizer for the photolysis of CH_3ReO_3 by the intervention of a new excited state. LLCT excitation is apparently followed by deactivation to the $CH_3^- \rightarrow Re^{VII}$ LMCT state, which reacts in the same way as the LMCT state of the parent compound CH_3ReO_3 [13,14].

2.3. Metal-to-metal charge transfer (MMCT)

Upon addition of $[Fe(CN)_6]^{4-}$ to aqueous $MeReO_3$, the solution turns red–brown. This color is attributed to the binuclear complex $[CH_3Re^{VII}O_3(\mu\text{-}NC)Fe^{II}(CN)_5]^{4-}$ [23]. The new absorption band at $\lambda_{max} = 437$ nm is assigned to a $Fe^{II} \rightarrow Re^{VII}$ MMCT transition. In solution the binuclear complex is not very stable ($K = 263\ M^{-1}$) and dissociates partly into its mononuclear components. Upon long-wavelength irradiation ($\lambda_{irr} > 390$ nm) the binuclear complex undergoes a photodecomposition with formation of $[Fe(CN)_6]^{3-}$. MMCT excitation generates a redox isomer, which undergoes secondary reactions including an irreversible decay of the $[CH_3Re^{VI}O_3]^-$ fragment:

$$[CH_3Re^{VII}O_3(\mu\text{-}NC)Fe^{II}(CN)_5]^{4-} \xrightarrow{h\nu} [CH_3Re^{VI}O_3(\mu\text{-}NC)Fe^{III}(CN)_5]^{4-}$$

$$[CH_3Re^{VI}O_3(\mu\text{-}NC)Fe^{III}(CN)_5]^{4-} \rightarrow [CH_3Re^{VI}O_3]^- + [Fe^{III}(CN)_6]^{3-}$$

Photoredox reactions of binuclear ligand-bridged metal complexes induced by MMCT excitation have been studied for nearly two decades [24]. A variety of oxidizing metal centers are known to participate in MMCT. However, it is quite intriguing that d^0 metals have been rarely observed to function as acceptors for MMCT transitions. A unique example has recently been described by Kaim et al. [25]. The mixed-valence complexes $[Cl(CO)_3Re^I(\mu\text{-}S)_2Re^{VII}S_2]^-$ and $[Cl(CO)_3Re^I(\mu\text{-}S)_2Re^{VII}(\mu\text{-}S)_2Re^I(CO)_3Cl]^-$ show $Re^I \rightarrow Re^{VII}$ MMCT absorptions which appear at rather long wavelength ($\lambda_{max} = 500$ and 600 nm, respectively).

2.4. Intraligand (IL)

The solid adduct CH_3ReO_3·*trans*-4-styrylpyridine shows its longest-wavelength absorption at $\lambda_{max} = 342$ nm which is assigned to an IL π–π^* absorption of styrylpyridine [26]. An additional $CH_3^- \rightarrow$ styrylpyridine LLCT band at longer wavelength was not detected. The π^* orbitals of styrylpyridine are apparently too high in energy. In solution (e.g. CH_2Cl_2) the adduct dissociates and partially releases styrylpyridine. Nevertheless, upon irradiation with 366 nm-light a selective IL excitation of the coordinated styrylpyridine of the intact adduct is possible since the free ligand absorbs at somewhat shorter wavelength. The irradiation of the coordinated styrylpyridine at 366 nm leads to complete *trans* → *cis* isomerization of the ligand, while the photolysis of the free ligand, which requires shorter-wavelength irradiation (313 nm), yields a photostationary mixture with 88% of the *cis* isomer. Owing to the kinetic lability of the adduct its photolysis takes place as a photoassisted reaction of the ligand:

$$CH_3ReO_3 + \textit{trans}\text{-4-styrylpyridine} \rightleftarrows CH_3ReO_3(\textit{trans}\text{-4-styrylpyridine})$$

$$CH_3ReO_3(\textit{trans}\text{-4-styrylpyridine}) \xrightarrow{h\nu/366\ \text{nm}} CH_3ReO_3(\textit{cis}\text{-4-styrylpyridine})$$

$$CH_3ReO_3(\textit{cis}\text{-4-styrylpyridine}) \rightleftarrows CH_3ReO_3 + \textit{cis}\text{-4-styrylpyridine}$$

$$\text{sum:}\quad \textit{trans}\text{-4-styrylpyridine} \rightarrow \textit{cis}\text{-4-styrylpyridine}$$

The photochemical behavior of $XRe(CO)_3$styrylpyridine [27] is quite similar to that of CH_3ReO_3styrylpyridine. However, the photoassisted *trans*/*cis* ligand isomerization is hampered by the kinetic stability of the Re(I) complex.

3. Rhenium(I) compounds

With regard to their excited state properties complexes of the type Re^I(1,2-diimine)$(CO)_3X$ with X = halide are organometallic analogues of $[Ru^{II}(bipy)_3]^{2+}$ [1,28–30]. Light-induced processes of these compounds have had a tremendous impact on inorganic and even photochemistry in general. The work on Re(I) complexes was initiated by Wrigthon's pioneering studies [1,31]. In the meantime many other groups have contributed to this subject. The main interest has been directed to the behavior of Re^I(1,2-diimine)$(CO)_3X$ compounds in their MLCT excited states. Since this subject has been reviewed extensively [1,28–30] only certain aspects will be mentioned here. In recent years the spectroscopy and photochemistry of Re(I) has been extended to other complexes in different excited states. In the following discussion these new developments will be emphasized.

3.1. Metal centered (MC)

All Re(I) complexes are pseudo-octahedral low-spin d^6 complexes. Simple Re(I) carbonyl halides such as $Re(CO)_5Cl$ ($\lambda_{max} = 341$ nm) show only LF absorptions at long wavelength [1,32]. MLCT transitions terminating at π^* (CO) orbitals require much higher energies. Solid $Re(CO)_5X$ with X = Cl, Br, I is luminescent but only at low temperatures. It is quite reasonable to attribute this emission to a phosphorescence which originates from the lowest-energy LF triplet [1,32]. Generally, metal carbonyls with lowest-energy LF excited states undergo a photosubstitution [1,2,33]. Indeed, the irradiation of $Re(CO)_5X$ leads to the release of a CO ligand which is finally replaced by the solvent or other suitable donor molecules [1,32]. The complex $C_5H_5Re^I(CO)_3$ ejects also a CO ligand upon LF excitation [1,34].

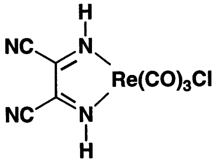
3.2. Ligand-to-metal charge transfer (LMCT)

LMCT absorptions have apparently not yet been identified in the absorption spectra of Re(I) carbonyl complexes [1].

3.3. Metal-to-ligand charge transfer (MLCT)

3.3.1. Absorption

Complexes of the type Re(1,2-diimine)$(CO)_3X$ with X = halide contain a reducing metal center and an acceptor ligand with low-energy π^* orbitals. Consequently, these compounds display long-wavelength MLCT ($Re^I \rightarrow$ diimine) absorptions in their electronic spectra [1,28,30]. These bands undergo a blue shift in more polar solvents (negative solvatochromism). The extent of this solvatochromism may be correlated with the degree of charge transfer. If metal and ligand orbitals are heavily mixed the 'MLCT' transition takes place between delocalized orbitals and only little charge transfer occurs [35]. Generally, this mixing increases with the decreasing energy of the diimine π^* orbitals. Accordingly, a variation of the diimine which leads to a red shift of the MLCT absorption is also associated with a reduced CT contribution. Indeed, the complex Re(diiminosuccinodinitrile)$(CO)_3Cl$ which shows its MLCT bands at rather long wavelength (~ 550 nm) is only slightly solvatochromic (Fig. 2) [36].



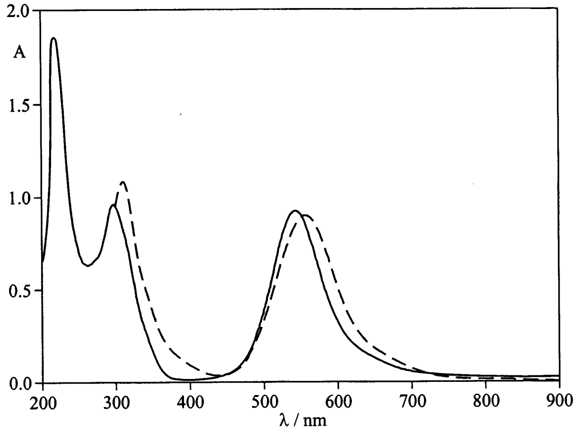
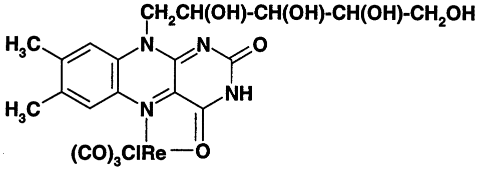


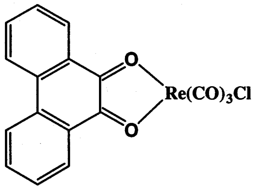
Fig. 2. Electronic absorption spectra of Re(diiminosuccinodinitril)(CO)$_3$Cl in acetonitrile (—, 1.52×10^{-4} M) and in benzene (- - -, 2.49×10^{-4} M) at r.t., 1-cm cell.

Related acceptor ligands are obtained when the imino groups of 1,2-diimines are successively replaced by oxygen atoms [37]. Riboflavin (vitamin B$_2$) is a rather intriguing ligand of this type [38] because it is one of the most important organic redox coenzymes. It participates in biological electron transfer with redoxactive metalloenzymes. Accordingly, the nature of flavin metal complexes is of considerable interest [38]. The complex Re(riboflavin)(CO)$_3$Cl shows its MLCT absorption ($\lambda_{max} = 556$ nm) [39].



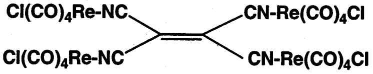
The solvatochromism is rather small indicating only partial charge transfer.

The replacement of both imino groups of 1,2-diimines by oxygen atoms leads to 1,2-diketones or *ortho*-quinones. Quinone complexes are of particular interest since quinones are the primary electron acceptors in natural photosynthesis. Unfortunately, quinone complexes apparently are not very stable. Nevertheless, the complex Re(9,10-phenanthrene-quinone)(CO)$_3$Cl was prepared and characterized [40].



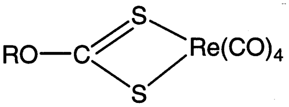
The Re→quinone MLCT absorption appears at $\lambda_{max} = 553$ nm (in CHCl$_3$) while the corresponding diimine complex Re(9,10-phenanthrenequinone diimine)(CO)$_3$Cl shows its MLCT band at $\lambda_{max} = 711$ nm [40]. It follows that the quinone is clearly a stronger acceptor than its diimine.

TCNX (tetracyanoethylene, TCNE and tetracyanoquinodimethane, TCNQ) is a powerful acceptor which can also coordinate to metals [41]. The reaction with $Re(CO)_5Cl$ yields the tetranuclear complexes $TCNX[Re(CO)_4Cl]_4$ [42], e.g.



As expected the Re → TCNX transitions occur at very low energies. The MLCT absorptions appear only in the near IR at $\lambda_{max} = 900$ nm (TCNE) and 990 nm (TCNQ). In this context it has been noticed that these complexes might serve as center units for dendrimers [42]. Owing to the low MLCT energies, electron as well as energy transfer could be driven from the periphery to the inner core of the dendrimer.

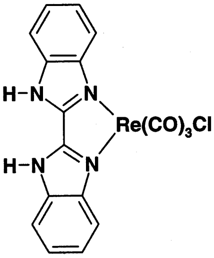
Organic sulfur compounds which contain C=S double bonds are also potential acceptor ligands because their π* orbitals should occur at relatively low energies owing to the weak C–S π overlap. The complex $Re^I(CO)_4$(xanthate) confirms this expectation [43]. A Re → xanthate MLCT absorption is observed at $\lambda_{max} = 327$ nm.



All ligands discussed above provide π* acceptor orbitals. However, it is also feasible that MLCT transitions terminate at σ* orbitals [44]. Generally, σ* orbitals are too high in energy but in certain cases (e.g. halogens, peroxide, disulfide) the σ* orbitals are located at accessible energies. Such ligands may act as acceptors for low-energy MLCT transitions. The complex $Re^I_2(PhSe{-}SePh)(CO)_6Br_2$ shows such an MLCT ($Re^I \rightarrow \sigma^*$ Se_2Ph_2) absorption at $\lambda_{max} = 446$ nm (in cyclohexane) [45].

3.3.2. Emission

The immense attention which has been paid to Re(1,2-diimine)$(CO)_3Cl$ compounds is based on their excited state properties. In analogy to $[Ru(bipy)_3]^{2+}$ many of these rhenium complexes show an emission which originates from the lowest-energy MLCT triplet. This phosphorescence which appears in solution at room temperature (r.t.) can be quenched by electron and energy transfer. The reader is referred to various reviews which cover all aspects of this subject [1,28,30]. Recently, we have studied the luminescence spectra of Re(1,2-diimine)$(CO)_3Cl$ complexes which contain diimines with imidazole subunits [46], e.g.:



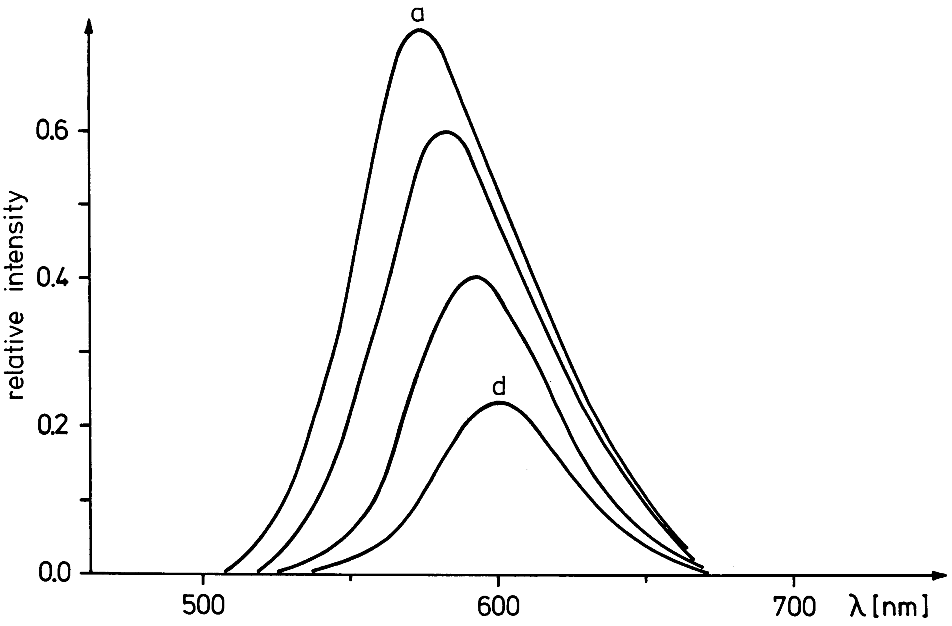
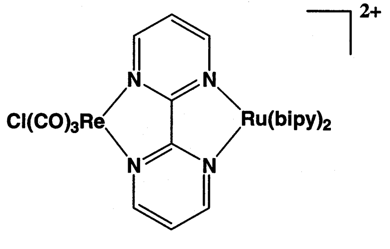


Fig. 3. Emission spectra of 1.5×10^{-4} M Re(4,7-diphenyl-1,10-phenanthroline)$(CO)_3Cl$ in decaline in the presence of (a) 0 M; (b) 8×10^{-4} M; (c) 2×10^{-3} M; and (d) 8×10^{-3} M *N*,*N*-dimethylaniline, 1-cm cell.

It was the aim of this work to evaluate the MLCT emission as a probe for biological systems. However, imidazoles are only weak electron acceptors. Accordingly, the MLCT luminescence appears at rather short wavelength [46].

Although emission quenching of Re(1,2-diimine)$(CO)_3Cl$ complexes by electron transfer can be quite efficient in polar solvents an exciplex emission may be observed in non-polar solvents [47]. The luminescence of Re(4,7-diphenyl-*o*-phen)$(CO)_3Cl$ in acetonitrile is completely quenched by excited-state electron transfer from dimethylaniline (DMA). On the contrary, in decaline solutions a new red-shifted emission appears which is attributed to the ion pair $DMA^+Re(diimine)(CO)_3Cl^-$ (Fig. 3). In polar solvents this exciplex emission is absent owing to a facile solvation of the ions.

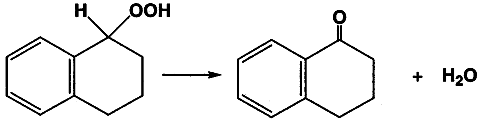
Recently, the emission behavior of polynuclear 1,2-diimine rhenium(I) carbonyl complexes has attracted much attention. This interest is also related to potential applications in supramolecular chemistry including optical sensing [48,49]. In one of the first reports on the electronic spectra of polynuclear Re(I) diimine complexes we described our observation on the luminescence properties of $[Cl(CO)_3Re^I(2,2'\text{-bipyrimidine})Ru^{II}(bipy)_2]^{2+}$ [50].



Light absorption by the Re → bipyrimidine MLCT band is followed by energy transfer to the lower-lying Ru → bipyrimidine MLCT state which returns to the ground state by emission. These processes can also be explained as an excited-state electron transfer mechanism.

Emitting MLCT states of Re(1,2-diimine)$(CO)_3Cl$ complexes are not only accessible by light absorption but also by chemical reactions which provide enough energy for the population of the emitting state. This can be induced electrochemically [51]. For example, the electrolysis of Re(*o*-phen)$(CO)_3Cl$ leads to an oxidation and reduction. Back electron transfer from Re(*o*-phen)$(CO)_3Cl^-$ to Re(*o*-phen)-$(CO)_3Cl^+$ generates the neutral complex in the MLCT excited state. The subsequent emission is termed electrogenerated chemiluminescence (ECL).

An interesting variation of ECL which does not require electricity is based on the redox decomposition of tetralinyl hydroperoxide:



This reaction is catalyzed by Re(*o*-phen)$(CO)_3Cl$ [52]. It is suggested that this catalysis proceeds by an electron exchange mechanism between the peroxide and the rhenium complex. In the final step the oxidized complex Re(*o*-phen)$(CO)_3Cl^+$ is apparently reduced by the α-tetralone radical anion. The potential difference for this redox reaction is sufficient to generate the neutral complex in its emissive MLCT state (Fig. 4).

At this point it must be emphasized that there are also many Re(I) carbonyl complexes with lowest-energy MLCT states which are non-emitting. In some cases such MLCT states are inherently reactive (see below). In other cases the MLCT states are deactivated by radiationless decay to the ground state. This situation applies to complexes with MLCT states at rather low energies such as [Re(bisacetylbisanile)$(CO)_3Cl$] [36], riboflavin [39] and 9,10-phenanthrenequinone [40]. This lack of emission may be attributed to the energy gap law.

3.3.3. Photoreactivity

The MLCT states of $[Ru(bipy)_3]^{2+}$ and Re(bipy)$(CO)_3Cl$ are considered to be prototypes of excited states which are inert to ligand substitution. This stability is apparently associated with the nature of orbitals involved in the MLCT transition. Neither the dπ donor nor the π* (bipy) acceptor orbitals are engaged in strong M–L bonding or antibonding interactions. As a consequence, these MLCT states are not inherently reactive but strongly emissive. Of course, these MLCT states are susceptible to electron or energy transfer. This type of photoactivity has been studied extensively. Various applications are feasible. For example, CO_2 can be reduced photochemically with Re(I) diimine complexes as catalysts [53–58]. The MLCT excited state participates in electron transfer as the primary photochemical step.

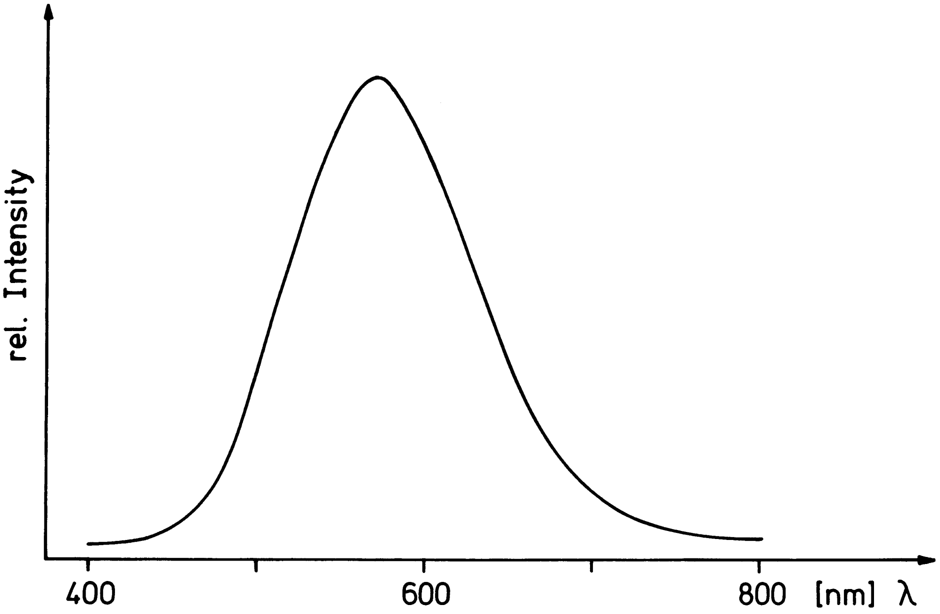


Fig. 4. Chemiluminescence spectrum recorded during the decomposition of tetralinyl hydroperoxide catalyzed by Re(*o*-phen)$(CO)_3Cl$ at 180°C, 1-cm cell.

However, certain Re(I) carbonyl complexes with suitable acceptor ligands may have available MLCT states which are intrinsically reactive. This behavior is illustrated by the complex $Re^I(CO)_4$(xanthate) which undergoes a decomposition upon $Re \rightarrow \pi^*$ (xanthate) MLCT excitation [43]. The reduction of xanthate is apparently an irreversible process leading to product formation. This photolysis can be viewed as a model for the photochemical reduction of carbonate. A direct optical CT involving CO_3^{2-} as acceptor has not yet been observed. It is expected to require rather high energies since carbonate is hardly oxidizing. However, if the oxygen atoms of carbonate or esters of carbonic acid are replaced by sulfur the π^* energies are lowered considerably [43]. Accordingly, it is not surprising that the photolysis of $Re(CO)_4$(xanthate) is induced by MLCT excitation with near-UV light.

The binuclear complex $Re_2(Se_2Ph_2)(CO)_6Br_2$ is also light sensitive [44,45]. Since the MLCT transition terminates at the σ^* (Se – Se) orbital of the Se_2Ph_2 ligand an intramolecular oxidative addition could take place:

$$Re_2^I(Se_2Ph_2)(CO)_6Br_2 \rightarrow 2\ Re^{II}(SePh)(CO)_3Br$$

Unfortunately, the photoproducts were not identified. However, related thermal reactions are well known [45].

3.4. Ligand-to-ligand charge transfer (LLCT)

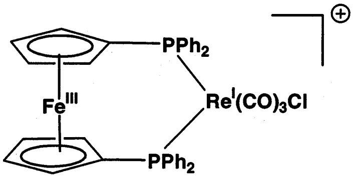
The lowest-energy excited state of Re(1,2-diimine)$(CO)_3X$ may switch from MLCT to $X^- \rightarrow$ diimine LLCT if X^- is a strong donor and provides the HOMO for the complex. Suitable candidates are the more reducing halides Br^- and I^- as well as carbanions. While the halide complexes are emissive the alkyl compounds are reactive [22]. In the latter case LLCT excitation involves an electron transfer from the rhenium–carbon σ-bond to the π* orbital of the diimine. Accordingly, the Re–C bond undergoes homolysis in the primary photochemical step [22].

LLCT excited states also play an important role in chromophore-quencher molecules of the general composition Re^I(1,2-diimine)$(CO)_3$(donor)$^+$ with donors such as 4-dimethyl-aminobenzonitrile [28,59]. The MLCT luminescence is quenched by electron transfer from the donor to Re^{II}. The resulting donor to diimine LLCT state is, however, not reactive owing to a facile return to the ground state. The LLCT state is not observed in absorption.

3.5. Metal-to-metal charge transfer (MMCT)

Polynuclear complexes which simultaneously contain a reducing and an oxidizing metal center can show optical MMCT [24,60–63]. Frequently, the metals are bridged by cyanide which facilitates the metal–metal interaction. Recently, such complexes with Re(I) as donor and Fe(III) as acceptor have been prepared and characterized. For example, the anion [4,4′-dimethyl-2,2′-bipyridine)$(CO)_3Re^I\mu$-$NCFe^{III}(CN)_5]^{2-}$ displays its $Re^I \rightarrow Fe^{III}$ MMCT absorption at $\lambda_{max} = 613$ nm (in water) [64]. The energy of this band strongly depends on the solvent.

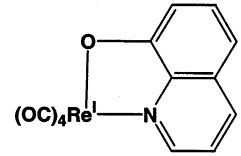
In the complex $[Fe^{III}(C_5H_4PPh_2)_2Re^I(CO)_3Cl]^+$ both metals are bridged in a quite different fashion.



This complex shows also a $Re^I \rightarrow Fe^{III}$ MMCT absorption ($\lambda_{max} = 700$ nm, in CH_2Cl_2) [65]. A band analysis led to the conclusion that the metals are only weakly coupled. This interaction may take place through bonds or space. The binuclear complex is not light sensitive although MMCT states are quite reactive in other cases [24].

3.6. Intraligand (IL)

The electronic spectra of Re(1,2-diimine)$(CO)_3Cl$ complexes do not only show long-wavelength MLCT absorptions but also π–π* diimine IL bands [1,28,29]. Frequently, IL bands appear at shorter wavelength than MLCT absorptions. Occasionally, IL and MLCT bands occur in the same energy region. An unambiguous distinction may then be quite difficult. Some ligands with low-energy π–π* transitions are weak π-acceptors owing to the high energy of their π* orbitals. Any interference by MLCT transitions is then avoided and only IL absorptions appear at long wavelength. A ligand which meets this criterion is the 8-quinolinate (oxinate) anion. A variety of oxinato complexes show IL absorptions in the visible region [66]. The complex $Re^I(CO)_4$(oxinate) displays this IL band ($\lambda_{max} = 422$ nm) as longest-wavelength absorption (Fig. 5) [67].



Low-energy MLCT bands are not observed. The complex shows a weak IL fluorescence at $\lambda_{max} = 515$ nm and strong IL phosphorescence at $\lambda_{max} = 653$ nm in solution at r.t. While the fluorescence is not affected by oxygen the phosphorescence is completely quenched in air-saturated solutions. This oxygen quenching even takes place with solid $Re(CO)_4$(oxinate). As a result an application as an oxygen sensor is feasible.

Another example of a Re(I) compound with a lowest-energy IL triplet is the complex $Re(CO)_4$(bzq) which contains the deprotonated benzo[h]quinoline (bzq) as ligand [68].

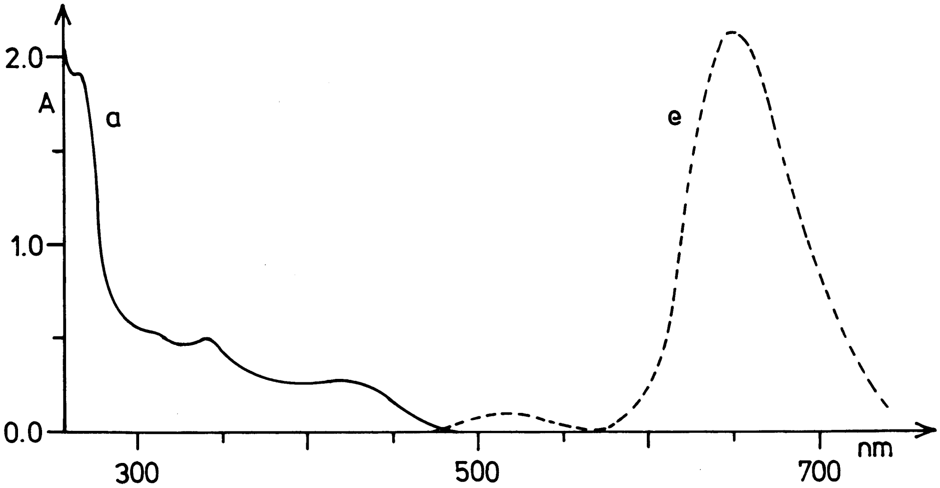
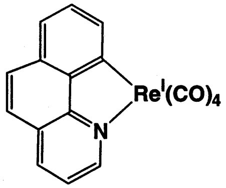


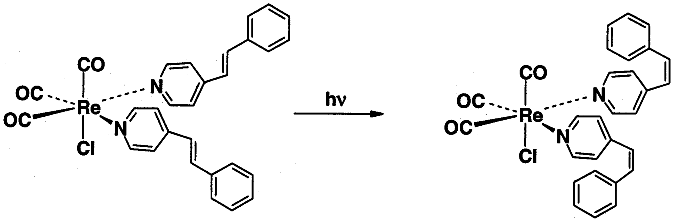
Fig. 5. Electronic absorption (a, —) and emission (e,- - -) spectra of 1.31×10^{-4} M $Re(CO)_4$(oxinate) in CH_3CN at r.t., 1-cm cell. Emission: $\lambda_{exc} = 440$ nm, intensity in arbitrary units.



While the complex is not fluorescent it shows a structured and long-lived (4.7 ms at 77 K and 6.4 μs at r.t.) IL phosphorescence. The IL triplet is susceptible to bimolecular quenching. Again, the phosphorescence is completely absent in air-saturated solution.

Generally, the reactivity of the IL excited states resembles that of the free ligand. Since free ligands are frequently not light sensitive IL excitation of the corresponding complex is also not accompanied by a photoreaction. Of course, bimolecular processes such as excited-state electron or energy transfer can still take place. They might be even favored since IL triplets are rather long-lived compared to other excited states of the complex. This behavior is illustrated by the phosphorescence quenching mentioned above. Energy transfer may lead to the generation of singlet oxygen. This assumption follows from the photosensitivity of $Re(CO)_4$(oxinate) in air-saturated solutions [67]. Singlet oxygen could oxidatively attack the complex.

In the case of Re(*trans*-4-styrylpyridine)$_2(CO)_3Cl$ the photochemical behavior is similar to that of the free styrylpyridine [27].



The *trans*/*cis* isomerization at the olefinic double band is initiated by π–π* excitation within the ligand. It is remarkable that this IL excited state can also be generated by electricity ('electrochemically induced photochemistry') [69]. In analogy to ECL the electrolysis by an alternating current leads to an oxidation and reduction of the complex. The subsequent cation–anion annihilation provides enough energy to generate the complex in its lowest-energy IL excited state which undergoes a ligand isomerization as it also takes place photochemically.

The complex Re(phenylhydrazine)$_2(CO)_3Cl$ represents another example of a reactive IL state [70]. The photolysis of the complex as well as that of the free phenylhydrazine proceeds according to the equation

$$2PhNH\text{–}NH_2 \rightarrow C_6H_6 + N_2 + Ph\text{–}NH_2 + NH_3$$

The photochemistry of the free ligand is apparently preserved in the complex because the electronic structure of phenylhydrazine is only slightly modified by coordination.

4. Conclusion

Organometallic Re(VII) and Re(I) compounds are characterized by a large diversity of excited states which may be luminescent or reactive. Many interesting applications can be anticipated. For example, CH_3ReO_3 is itself an important catalyst [17]. So it is feasible that this catalytic activity is modified photochemically. Quite different applications could be based on the excited state properties of Re(I) complexes. Charge separation by MLCT or LLCT excitation may lead to novel solar energy conversion systems [71]. Excited-state electron transfer can be utilized for CO_2 reduction [53–58]. Luminescence quenching of MLCT and IL states might be applied for oxygen sensing [72]. Moreover, molecular squares and rectangles which consist of Re(I) carbonyl fragments are able to selectively bind anionic guests [48,49]. Again, optical sensors are conceivable. Such supramolecular applications could be extended to dendrimers which are based on Re(I) carbonyl core units [42].

In this context it is appropriate to emphasize some further attractive features of rhenium(I) carbonyl complexes including Re(1,2-diimine)$(CO)_3Cl$ compounds. The preparation is very simple. Frequently, it is sufficient to heat $Re(CO)_5Cl$ and a potential ligand in a suitable solvent for a few minutes. The desired compound precipitates upon cooling. The compounds are soluble in solvents of quite different polarity. In addition, the solvato-chromism of Re(1,2-diimine)$(CO)_3Cl$ complexes can be used as an environmental probe in heterogeneous media including biological systems. In addition, since their luminescence depends on the viscosity of the medium emissive Re(1,2-diimine)$(CO)_3Cl$ complexes are utilized to probe structural features of polymers [73].

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