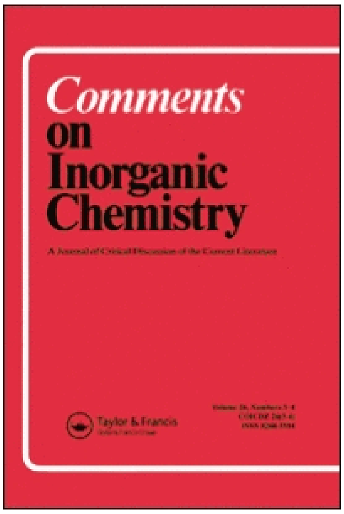

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

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D. J. Stufkens[a]
[a] Anorganisch Chemisch Laboratorium, University of Amsterdam, WV Amsterdam, The Netherlands

To cite this Article Stufkens, D. J.(1992) 'The Remarkable Properties of α-Diimine Rhenium Tricarbonyl Complexes in Their Metal-to-Ligand Charge-Transfer (MLCT) Excited States', Comments on Inorganic Chemistry, 13: 6, 359 — 385
To link to this Article: DOI: 10.1080/02603599208048467
URL: http://dx.doi.org/10.1080/02603599208048467

The Remarkable Properties of α-Diimine Rhenium Tricarbonyl Complexes in Their Metal-to-Ligand Charge-Transfer (MLCT) Excited States

D. J. STUFKENS
Anorganisch Chemisch Laboratorium,
University of Amsterdam,
Nieuwe Achtergracht 166,
1018 WV Amsterdam,
The Netherlands

Received April 15, 1992

α-Diimine rhenium tricarbonyl complexes $[(L)Re(CO)_3(\alpha\text{-diimine})]^{0/+}$ are exceptional among organometallic complexes in showing emission from their MLCT states at room temperature in fluid solution. The properties of these states can be "fine-tuned" by variation of the α-diimine and co-ligand L, the solvent and the rigidity of the medium. Light-induced energy and electron transfer processes occur inter- and intramolecularly. Reductive quenching of the MLCT state leads to a charge-separated LLCT state. The excited state properties of these chromophore–quencher complexes seem to be related to those of the binuclear metal–metal bonded complexes $[L_nMRe(CO)_3(\alpha\text{-diimine})]$ (L_nM = metal fragment).

Key Words: *α-diimines, rhenium tricarbonyls, metal-to-ligand charge transfer, emission, ligand-to-ligand charge transfer, energy and electron transfer, ligand-bridged complexes, metal–metal bonded complexes, chromophore–quencher complexes*

Abbreviations Used: *bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline, bpm = 2,2'-bipyrimidine, bpp = 2,3-bis(2-pyridyl)pyrazine, py = pyridine, pyz = pyrazine, Im = imidazole, DAB = 1,4-diaza-1,3-butadiene, PyCa = pyridine-carbal-*

Comments Inorg. Chem.
1992, Vol. 13, No. 6, pp. 359–385
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dimine, Ph = phenyl, Me = methyl, Et = ethyl, Bz = benzyl, PTZ = phenothiazine, iPr = iso-propyl, pTol = para-tolyl, Cp = η^5-C_5H_5

INTRODUCTION

Only few luminescence data of organometallic complexes have been reported prior to the mid 1970s.[1] Since then there has been a rapidly growing interest in the excited state properties of such complexes.[2] Most attention was paid to complexes having a long-lived metal-to-ligand charge-transfer (MLCT) state which appeared to be good photosensitizers for light-induced energy and electron transfer processes. $Ru(bpy)_3^{2+}$ and its derivatives have been most widely used for this purpose,[3-8] but the organometallic complex *fac*-$[ClRe(CO)_3(bpy)]$ and its derivatives have also obtained much attention in this respect. The excited state properties of these Re-complexes can be "fine-tuned" both by varying the α-diimine ligand and by replacing the chloride ion by a great variety of ligands. Such a ligand may only shift the MLCT state, but it can also act as an oxidative or reductive quencher, as a bridging ligand, or as an extra chromophoric group. These variations in the excited state properties of a large series of these complexes $[(L)Re(CO)_3(L\text{-}L)]^{o/+}$ (L-L = α-diimine such as bpy, phen, etc.; L = halide, N-donor, bridging ligand, chromophore, organic donor/acceptor) will be discussed in this article. Finally, the results obtained for the organic donor (D)-substituted complexes $[(D)Re(CO)_3(L\text{-}L)]^+$ will be related to the excited state properties of the metal–metal bonded complexes $[L_nMRe(CO)_3(L\text{-}L)]$ (L_nM = $(CO)_5Mn$, $(CO)_5Re$, $(CO)_4Co$, etc.) which we are currently investigating. The structure of the complexes $[(L)Re(CO)_3(L\text{-}L)]^{o/+}$ is shown in Fig. 1.

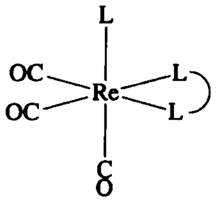


FIGURE 1 Structure of the complexes *fac*-$[(L)Re(CO)_3(L\text{-}L)]$.

ABSORPTION SPECTRA

The low-spin d^6 complexes $[(L)Re(CO)_3(L\text{-}L)]^{0/+}$ are characterized by intense MLCT transitions between 350 and 500 nm, depending on the α-diimine ligand L-L, the co-ligand L and the solvent used.[9-13] The MLCT band maximum shifts to higher energy in more polar or polarizable solvents and its position depends on the energy of the lowest π* orbital of the α-diimine ligand. The MLCT character of the first absorption band is also evident from the resonance Raman spectra, obtained by excitation into this band.[10]

EMISSION SPECTRA

Wrighton and Morse were the first to recognize that the complexes $[ClRe(CO)_3(L\text{-}L)]$ are exceptional among the metal carbonyls in showing emission in room temperature fluid solution[9] (Fig. 2). The emission lifetimes were typical of complexes having a lowest MLCT state. Contrary to the absorption maxima, the emission maxima were hardly solvent dependent. The MLCT character of the lowest

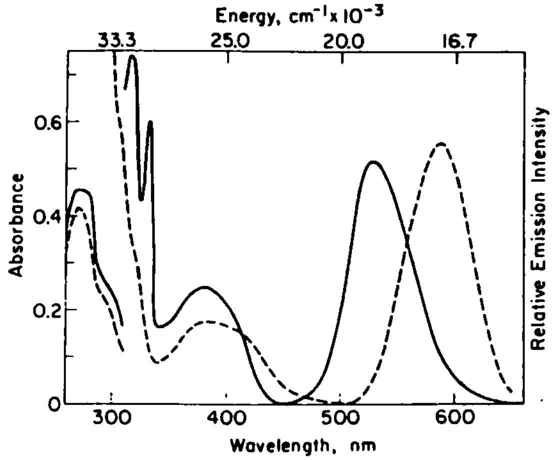


FIGURE 2 Absorption (left) and emission (right) of $[ClRe(CO)_3(phen)]$ in EPA at 298 K (– – –) and 77 K (—) (from Ref. 9).

excited state was evident from the excited-state Raman spectra obtained by excitation of $[XRe(CO)_3(bpy)]$ ($X = Cl,Br$) with the 355 nm line of a Nd:YAG laser.[14] Fast time-resolved IR spectra of the closely analogous complex $[ClRe(CO)_3(4,4'\text{-bipyridyl})_2]$ were consistent with this assignment since the $\nu(CO)$ bands appeared to shift to higher frequency upon excitation.[15] Replacement of the chloride ion by another nonchromophoric ligand such as PR_3 or a N-donor ligand had a distinct influence on the emission properties. With respect to the corresponding chloride complex the emission maximum of, e.g., $[(CH_3CN)Re(CO)_3(phen)]^+$ shifted to higher energy as a result of the lowering of electron density on Re.[16] Although the emission of this complex ion still has MLCT character at room temperature, the emission band consisted of two emission features at 77 K in EPA with lifetimes of 11 and 75 μs, respectively.[16] These features were assigned to MLCT emission and to intraligand (IL) emission of the α-diimine ligand, respectively. The change in emission properties is a result of the general phenomenon that MLCT states shift to higher energies going from room temperature fluid solution to low temperature glasses, whereas IL states are hardly influenced (Fig. 3A). As a result, these states, being different in energy at room temperature, may coincide at 77 K. The origin of this so-called "rigidochromic" effect on MLCT states will be discussed later. Other nitrogen-donor ligands gave similar results and the relative importance of the IL emission decreased when a more basic ligand was used or the temperature was raised.[16] Apparently, internal conversion between the IL and MLCT states is slowest when these states are close in energy, consistent with the geometrical difference of these two states. An

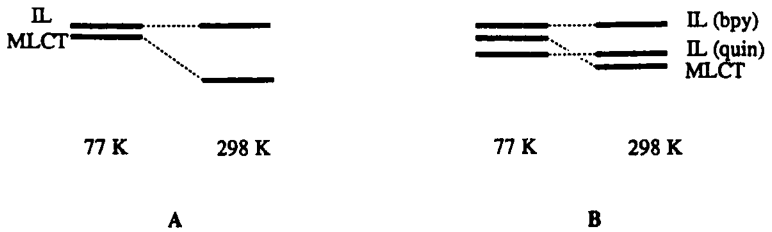


FIGURE 3 State diagram for the lowest excited states of $[(CH_3CN)Re(CO)_3(phen)]^+$ (A) and $[(quinoline)Re(CO)_3(bpy)]^+$ (B).

increase of energy separation will strengthen the vibronic coupling because of a greater density of states and only MLCT emission is then observable. A similar change from MLCT to IL emission upon cooling to 77 K was observed for the complexes [XRe(CO)$_3$L$_2$] (L = 4-phenylpyridine[17] or 3-benzoylpyridine[18]; X = halide). However, the 4-phenylpyridine complex only showed one long decay time at 77 K whereas the 3-benzoyl-pyridine complex again showed two different lifetimes. The mixed character of the emission of the 4-phenylpyridine complex was evident from the change of k_r with temperature. More recent studies have shown that by making a good choice of the α-diimine ligand, MLCT emission at room temperature transforms into pure IL, mixed IL/MLCT or dual IL/MLCT emission at 77 K depending on the relative energies of the states and the rate of internal conversion between them.[11,12,19] As a result, the emission properties at 77 K can be grouped into three classes: (i) the emission has more or less pure MLCT character since it is not structured and its lifetime is in the range 1–50 μs; (ii) the emission has mixed MLCT/IL character since it is structured and has one lifetime in the range 250–500 μs; (iii) the emission originates from both the MLCT and IL states since it is structured and can be resolved into a short-lived (ca. 10 μs) and a long-lived (50–500 μs) component.[11] In one case the α-diimine complex was observed to emit from an IL state already at room temperature.[19]

In the complex ion [(quinoline)Re(CO)$_3$(bpy)]$^+$ the quinoline is a chromophoric ligand. At room temperature this complex showed the normal MLCT emission, but at 77 K IL emission of the quinoline was observed[12] (Fig. 3B).

An interesting behaviour was observed for the complex ions [(NC(CH$_2$)$_n$CH$_3$)Re(CO)$_3$(bpy)]$^+$ in which n varied from 0 to 17.[20,21] The room-temperature emission lifetimes strongly depended on n. For small values of n, τ was virtually independent of chain length, but an abrupt increase of lifetime was observed over the range $7 \leq n \leq 13$. For still longer chain lengths, τ was nearly constant. These changes with increasing n were attributed to an intramolecular fold-back of the alkyl chain onto the bipyridine ligand. The displacement of solvent molecules changes the local environment of the complex and therefore also the energies of the MLCT states. The accompanying changes in lifetime appeared to be connected with a reduction of k_{nr}. Since the plot of lnk_{nr} vs. emission energy was linear, the changes in lifetime were attributed to an energy-gap law effect. A similar influence of the energy-gap law, reflected in a linear relationship between lnk_{nr} and the emission energy was found by Caspar and Meyer for a series of complexes $[(L)Re(CO)_3(bpy)]^{o/+}$ (L = Cl^-, N-donor ligand, PMe_3)[22] (Fig. 4). Such a relationship will, however, only hold for a series of closely related chromophores in a common solvent.

During their investigation of the emission spectra of a series of $[ClRe(CO)_3(L\text{-}L)]$ complexes, Wrighton and Morse observed a large shift to higher energy of the emission maxima going from fluid to rigid media[9] (Fig. 2). The origin of this *rigidochromic* effect was not clear at the time. Later studies showed this effect to be a general phenomenon, and for many polypyridyl complexes of Ru(II) and Os(II), discontinuities were found in the emission properties of MLCT states between fluid and glassy states. Balzani *et al.* studied the changes in emission lifetimes induced by the glass-to-fluid transition of several mixed-ligand polypyridine–Ru(II) complexes and they ascribed the observed variations to the effect of viscosity changes on low frequency Ru–N stretching and bending vibrations.[23] Tazuke and co-workers studied the time-resolved emission spectra at the glass-to-fluid transition of the complexes

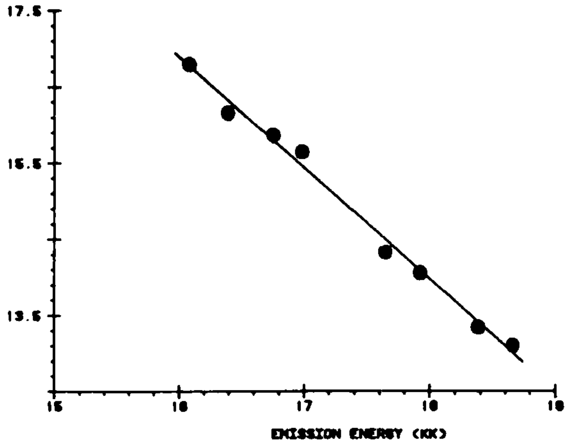


FIGURE 4 Plot of ln k_{nr} vs. E_{em} for the MLCT excited states of $[(L)Re(CO)_3(bpy)](PF_6)$ complexes at 296 K in CH_2Cl_2 (from Ref. 22).

[Ru(bpy)$_3$Cl$_3$] and *cis*-[Ru(bpy)$_2$(CN)$_2$].[24] The emission maximum of each complex shifted to the red with the delay time as well as with the increase in temperature in the glass-to-fluid transition region. The rate of the time-dependent red shift increased with temperature. This effect was ascribed to relaxation from a charge-delocalized excited state to a charge-localized excited state. Krausz had explained the changes in the excited-state resonance Raman spectra of [Ru(bpy)$_3$]$^{2+}$ in passing from the solid to the fluid phase with a similar charge localization effect.[25] This explanation can, however, not hold for the Re-complexes for which no such delocalization effects can occur. In fact, a similar time-dependent red shift was observed by Meyer and co-workers for the emission maximum of the complex ion [Os(phen)(das)$_2$]$^{2+}$ (das = 1,2-dimethylarsinobenzene) in 4:1 ethanol—methanol (v/v) solution at 130 K.[26] At this temperature the emission maximum shifted to lower energy over the time interval 30 ns to 1 μs after the laser pulse (Fig. 5). Below 110 K and above 145 K no time dependence was observed. Meyer *et al.* explained this shift with reorientation of the solvent dipoles around the excited molecule. In fluid solution these reorientations are fast and the emission occurs from excited states that are in equilibrium with their surroundings. Near the

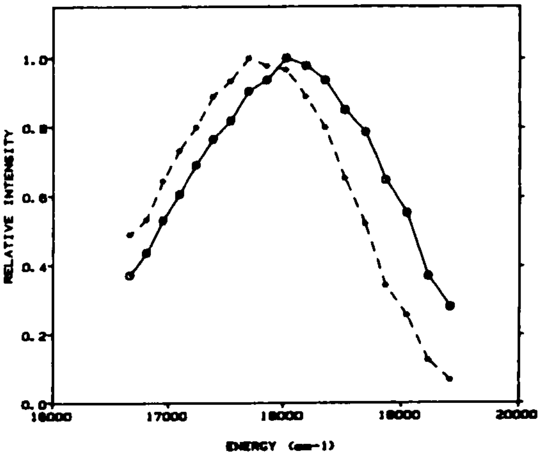


FIGURE 5 Time-resolved emission spectra of [Os(phen)(das)$_2$]$^{2+}$ in 4:1 ethanol–methanol (v/v) solution at 130 K. (○) 30 ns after excitation, (∗) 6 μs after excitation (from Ref. 26).

glass-to-fluid transition ($T \cong 130$ K) reorientation times become longer and are observable as a time dependence in the emission spectrum. Below 100 K the dipoles are frozen on the emission time scale; above 145 K reorientation of solvent dipoles is too rapid to observe a time dependence in the emission spectra.

Lumpkin and Meyer showed that the time- and temperature dependence of the emission properties in the glass-to-fluid transition region have the same origin.[27] They studied in detail the temperature dependence of the emission spectra of $[(py)Os(CO)(bpy)_2]^{2+}$ in an ethanol/methanol solvent mixture from 110 to 298 K. The majority of the temperature dependence was in E_{oo}, the energy gap between the excited and ground states. This behaviour is consistent with a situation in which the orientation of the surrounding solvent dipoles are intermediate between those in the glass and fluid solutions. The primary origin of the rigidochromic effect, first observed by Wrighton and Morse for the Re-complexes,[9] is therefore a difference in solvent dipole orientations between glass and fluid solution. Consistent with previous results for variations in solvent, counter ion and nonchromophoric ligand (*vide supra*), the changes in emission properties accompanying the glass-to-fluid transition were also in line with the energy-gap law.[27]

Quite recently, Lees and co-workers have used this sensitivity of the emission of Re-complexes to environmental rigidity to follow the cure process of epoxy resins.[19] For this purpose they added a small amount of a $[XRe(CO)_3(L\text{-}L)]$ (L-L = phen, Ph_2-phen, Me-phen, or Me_2-bpy; X = halide) complex to a solution of a model epoxide/anhydride system and studied the changes in emission intensity and lifetime of the Re-complex during the curing process. The emission increased approximately 10-fold when the epoxy system was cured and the emission lifetime changed from 280 ns to 4.1 μs.

INTERMOLECULAR ENERGY AND ELECTRON TRANSFER

Because of their long lifetimes the MLCT-excited complexes easily undergo intermolecular energy and electron transfer processes.

During their first experiments on the emission of a series of

$[ClRe(CO)_3(L\text{-}L)]$ complexes, Wrighton and Morse showed that the emission was quenched by oxygen, anthracene and trans-stilbene.[9] The quenching by trans-stilbene occurred with ~100% efficiency and resulted in trans → cis isomerization. Since the excited complexes are also more powerful reductants and better oxidants than the ground state species, intermolecular excited state electron transfer reactions can easily occur just as for $[Ru(bpy)_3]^{2+}$. Wrighton and co-workers studied the electron transfer quenching by N,N′-dimethyl-4,4′-bipyridinium (MV^{2+}) both with flash photolysis[29] and transient Raman spectroscopy.[30] The transient absorption spectra showed the typical electronic transition of MV^+ at ca. 600 nm which disappeared after a few milliseconds. The quenching rate constant was about diffusion controlled and decreased at higher reduction potential of the quencher. The formation of MV^+ was also evident from the transient Raman spectra of a mixture of MV^{2+} and $[ClRe(CO)_3(bpy)]$ in CH_3CN, excited with the 355 nm line of a Nd:YAG laser.[30] The Re-complexes are also powerful oxidants in their MLCT state and this was first demonstrated by Wrighton and co-workers for the reactions with a series of electron donors, mainly amines.[29] Again, the reactions were found to be diffusion controlled and the quenching rate constants decreased at higher oxidation potential of the quencher. In the case of the system $[ClRe(CO)_3(4,7\text{-}Ph_2\text{-phen})]$/N,N-dimethylamiline (DMA)

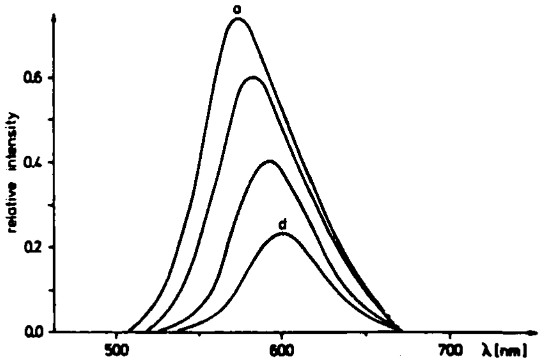


FIGURE 6 Emission spectra of $[ClRe(CO)_3(4,7\text{-}Ph_2\text{-phen})]$ in decaline in the absence of DMA (a), and in the presence of increasing concentrations of DMA (b–d).

electron transfer from DMA to Re caused the formation of the exciplex $[DMA^{\bullet +}Re(CO)_3(4,7\text{-}Ph_2\text{-}phen^{\bullet -})]^*$ which had its emission shifted to lower energy compared to the parent Re-complex[31] (Fig. 6). The emission was quenched by CH_3CN, which caused the exciplex to dissociate into ions. Exciplexes were also formed with other electron donors but not with electron acceptors. An interesting quenching reaction was observed by Wrighton *et al.* upon irradiation of the complexion $[(CH_3CN)Re(CO)_3(phen)]^+$ in the presence of excess PPh_3.[32] The emission was quenched and $[(PPh_3)Re(CO)_3(phen)]^+$ was formed with a quantum yield far exceeding 1. The reaction was proposed to proceed via (1)–(4):

$$[(CH_3CN)Re(CO)_3(phen)]^+ \xrightarrow{h\nu} [(CH_3CN)Re(CO)_3(phen)]^{+*}, \tag{1}$$

$$[(CH_3CN)Re(CO)_3(phen)]^{+*} + PPh_3 \rightarrow [(CH_3CN)Re(CO)_3(phen^{\bullet -})] + PPh_3^{+}, \tag{2}$$

$$[(CH_3CN)Re(CO)_3(phen^{\bullet -})] + PPh_3 \rightarrow [(PPh_3)Re(CO)_3(phen^{\bullet -})] + CH_3CN, \tag{3}$$

$$[(PPh_3)Re(CO)_3(phen^{\bullet -})] + [(CH_3CN)Re(CO)_3(phen)]^+ \rightarrow [(PPh_3)Re(CO)_3(phen)]^+ + [(CH_3CN)Re(CO)_3(phen^{\bullet -})]. \tag{4}$$

The emission is quenched by electron transfer from the phosphine producing the radical complex $[(CH_3CN)Re(CO)_3(phen^{\bullet -})]$ (reaction (2)). The unpaired electron of this radical mainly resides on the α-diimine (*vide infra*). Hard bases such as CH_3CN are only weakly bonded to the metal in these radicals and are easily replaced by PPh_3 (reaction (3)). This radical then reduces the complexion with formation of the reaction product $[(PPh_3)Re(CO)_3(phen)]^+$ and a new $[(CH_3CN)Re(CO)_3(phen^{\bullet -})]$ radical that starts the catalytic cycle (reaction (4)). Similar catalytic reactions occur when a metal–metal bonded complex such as $[(CO)_5MnRe(CO)_3(L\text{-}L)]$ is irradiated in the presence of PPh_3. No such catalytic reaction was observed when $[(CH_3CN)Re(CO)_3(phen)]^+$ was instead irradiated in the presence of pyridine. Substitution of CH_3CN by pyridine was, however, observed when N,N'-dimethyl-p-toluene was added to the solution as electron donor. The quantum yield of this reaction was, however, much lower than for the reaction with PPh_3.

Formation of a Re-radical complex also plays an essential role in the conversion of CO_2 into CO using a $[XRe(CO)_3(bpy)]$ (X = halide) complex as photosensitizer and catalyst.[33–37] The complexes were irradiated in the presence of triethanolamine (TEDA) as electron donor while bubbling CO_2 through the solution. The complete mechanism of this reaction is not yet clear, but certain aspects have been clarified. The initial photochemical step involves reductive quenching of the photoexcited complex by TEDA to give the rather stable radical complex $[XRe(CO)_3(bpy)]^{\cdot -}$. The bimolecular rate constant for this quenching reaction was the same in both Ar-bubbled and CO_2-bubbled solutions. This means that CO_2 does not interact with the MLCT excited Re-complex but reacts instead with the product of the quenching reaction. The yield of the radical complex correlated with the quantum yield of CO formation. This observation strongly supports the view that CO is produced by reaction of CO_2 with the radical complex $[XRe(CO)_3(bpy)]^{\cdot -}$. This latter reaction was followed with flash photolysis but the complex formed could only be characterized by its absorption band at 475 nm but not further be identified.[36] The factors that influence the CO formation have been studied in detail and a mechanism has been proposed, which, however, could not yet be proven.[34]

INTRAMOLECULAR ENERGY AND ELECTRON TRANSFER

Much attention has been paid recently to the construction of systems in which light-induced energy or electron transfer processes occur intramolecularly, preferably over long distances. Ligand-bridged homo- and heterobinuclear complexes have been studied as well as mononuclear chromophore–quencher complexes. The excited state properties of a few representative complexes will be discussed. It will also be shown that the metal–metal bonded complexes $[L_nMRe(CO)_3(L\text{-}L)]$ are most likely a special type of chromophore–quencher complexes.

Ligand-Bridged Complexes

In the complexes $[(L)Re(CO)_3(L\text{-}L)]^{0/+}$ both the α-diimine ligand L-L and the normally nonchromophoric ligand L can act as a bridge. In the first type of complexes simple tetradentate nitrogen donors such as 2,2′-bipyrimidine (bpm) or 2,3-bis(2-pyridyl)pyrazine (bpp) have been used but also more complicated molecules (Fig. 7).

Rillema and co-workers studied the emission spectra of the complexes $[(bpy)_2Ru(bpm)]^{2+}$, $[(bpy)_2Ru(bpmRe(CO)_3Cl)]^{2+}$, $[(bpy)Ru(bpmRe(CO)_3Cl)_2]^{2+}$, and $[Ru(bpmRe(CO)_3Cl)_3]^{2+}$.[38] The complexes only showed a weak emission which was Ru-based. The lifetimes of these emissions were rather long for the tri- and tetranuclear complexes (942 and 847 ns) compared to the mono- and binuclear compounds (76 and 131 ns).

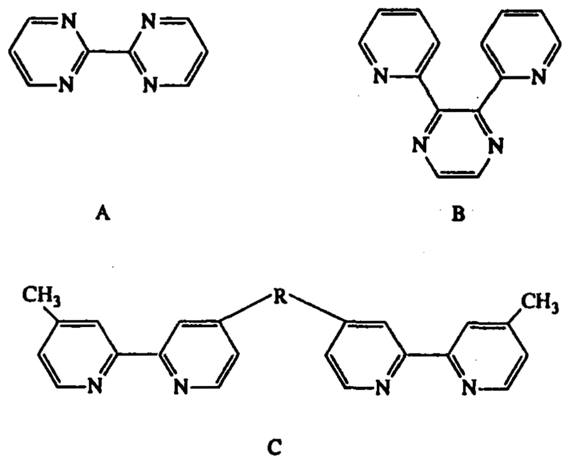


FIGURE 7 Bridging α-diimine ligands bpm (A), bpp (B) and Mebpy-R-Mebpy (C).

Rillema and co-workers also used the ligand Mebpy-R-Mebpy (R = CH_2CH_2) depicted in Fig. 7C as a bridge. The complexes [$ClRe(CO)_3$(Mebpy-R-Mebpy)] and [$(ClRe(CO)_3)_2$(Mebpy-R-Mebpy)] hardly differed in their absorption and emission properties.[39] Only the lifetime and quantum yield of the 600 nm emission decreased somewhat going from the mononuclear to the binuclear complex. Yet, there was clear evidence for light-induced energy transfer in the corresponding heterobinuclear complex [(py) $Re(CO)_3$(Mebpy-R-Mebpy)$Ru(bpy)_2]^{3+}$. Excitation into the visible absorption band of the Ru-fragment gave rise to the same emission as observed for the mononuclear complex ion [$(bpy)_2$Ru (Mebpy-R-Mebpy)$]^{2+}$. Only its lifetime (τ = 1191 ns) and quantum yield (ϕ = 0.119) had increased somewhat. Upon excitation with 355 nm into the absorptions of both metal fragments, the same Ru-based emission was again observed although with a shorter lifetime (τ = 1001 ns) and higher quantum yield (ϕ = 0.164). Normally, an increase in quantum yield is accompanied with an increase in lifetime and the deviating behaviour can only be caused by energy transfer from the Re- to the Ru-fragment. The energy transfer was also evident from the observation that 355 nm excitation only gave rise to emission from the Ru-fragment. The excitation spectra also showed peaks belonging to the Re-fragment which contributed to this emission. It is noteworthy that the emission spectrum of the complex first published by the authors in a communication[41] had a shoulder at the high-energy side of the Ru-emission which was not present in the corresponding spectrum of the full paper.[40] Apparently, this extra shoulder belonged to the emission of the complex ion [(py)$Re(CO)_3$(Mebpy-R-Mebpy)$]^+$ present as an impurity. Furue *et al.* have used the closely analogous molecule with R = $CH_2CH(OH)CH_2$ (Fig. 7C) as a bridging ligand in a series of binuclear complexes [(L)$Re(CO)_3$(Mebpy-R-Mebpy)$Ru(bpy)_2]^{n+}$ (L = Cl^-, 1-MeIm, 4-MePy,MeCN).[42] Again, only a Ru-based emission was observed upon 360 nm excitation with a very weak shoulder at its high energy side (Fig. 8). The shoulder was assigned to emission from the Re-fragment and energy transfer from Re to Ru was concluded to be nearly complete. The rate constant of intramolecular energy transfer ($=k_{en}$) was calculated from $k_{en} = k_{obs} - k_o$, in which k_{obs} and k_o were derived from the emission lifetime of the complex and the mononuclear

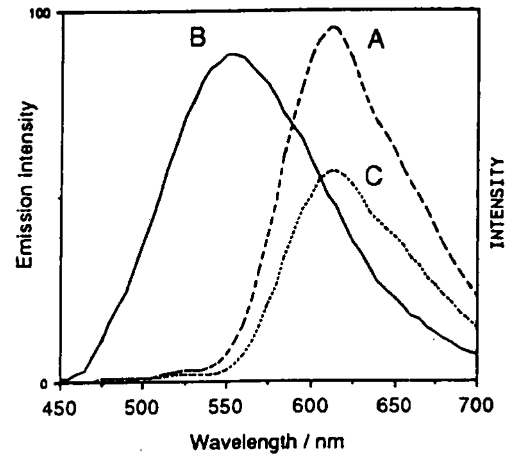


FIGURE 8 Emission spectra of [(4-MePy)Re(CO)$_3$(Mebpy-CH$_2$CH(OH)CH$_2$-Mebpy)Ru(byp)$_2$]$^{3+}$ (A) and [(4-MePy)Re(CO)$_3$(4,4'-Me$_2$-bpy)]$^+$ (B). Estimated contribution due to direct excitation of the complexion [Ru(bpy)$_2$(Mebpy-CH$_2$CH(OH)CH$_2$-Mebpy)$^{2+}$ (C) (from Ref. 42).

Re-compound, respectively. The values of k_{en} varied between 1.7 and 12×10^8 s^{-1}, depending on $\Delta G°$, the energy gap for the energy transfer reaction. $\Delta G°$ and as a result k_{en} could be influenced by varying the ligand L of the Re-fragment.

In the complexes [(L)Re(CO)$_3$(L-L)]$^{o/+}$, L normally represents a monodentate non-chromophoric ligand such as a halide or a nitrogen donor molecule (pyridine, CH$_3$CN). However, by using instead a ligand such as CN$^-$, pyrazine, or 4,4'-bpy, homo- and heterobinuclear complexes can and have been prepared. Pyrazine (pyz) was not a good choice since the complex ion [(CO)$_3$(bpy)Re (pyz)Re(CO)$_3$(bpy)]$^{2+}$ did not show any emission.[43] The pyz ligand acts as a trap since its π^* orbital is drastically lowered in energy by coordination of the two Re fragments. The Re → pyz MLCT state is then lowest in energy and this state is rapidly populated after initial irradiation into the Re → bpy MLCT transition. In the case of the 4,4'-bpy ligand, the character of the lowest excited state depends on the electronic properties of the α-diimine ligand used. Meyer and co-workers studied this effect for a series of binuclear Re-complexes having 4,4'-bipyridine as a bridge and 4,4'-substituted bipyridines as α-diimine ligands (Fig. 9).[44,45]

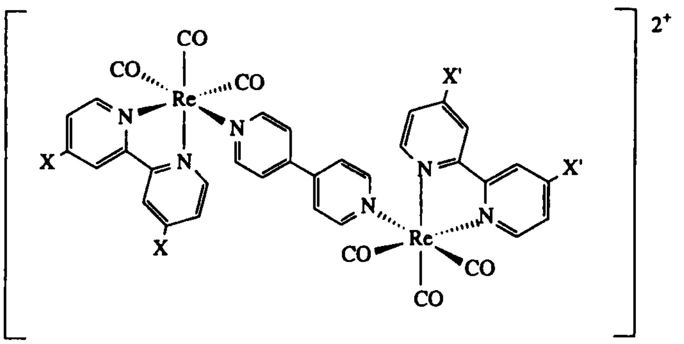


FIGURE 9 Schematic structure of [(4,4'-$(X)_2$-bpy)$(CO)_3$Re(4,4'-bpy)Re$(CO)_3$-(4,4'-$(X')_2$-bpy)]$^{2+}$.

For the complex having electron-withdrawing ester substituents (X = X' = CO_2Et) the transient absorbance spectrum, recorded 50 ns after excitation at 355 nm, showed absorptions at 380–390 nm and 460–480 nm which were also present in the transient absorbance spectrum of the model complex ion [(4-Etpy)Re$(CO)_3$(4,4'-$(CO_2Et)_2$-bpy)]$^+$. This means that the excited electron resides on the ester-substituted bpy ligand in the binuclear complex. Introduction of electron-donating amino groups in the bpy ligands (X = X' = NH_2) caused an inversion of the π^* levels. The transient absorbance spectrum showed absorptions at 570–590 nm and 390–400 nm. The low-energy band is characteristic for occupation of the lowest π^*-orbital of 4,4'-bpy and the lowest MLCT state is therefore a Re → 4,4'-bpy MLCT state. For the unsubstituted (X = X' = H) complex [(bpy)$(CO)_3$Re(4,4'-bpy)Re$(CO)_3$(bpy)]$^{2+}$ the Re → 4,4'-bpy and Re → bpy MLCT states appeared to be very close in energy and their relative energies were solvent dependent. In the asymmetric complex (X = H, X' = CO_2Et), the lowest excited state had Re → 4,4'-$(CO_2Et)_2$-bpy character and this state was formed within the laser pulse both by direct excitation and by energy transfer following Re → bpy excitation.

When instead of 4,4'-bpy, its 3,3'-Me_2-derivative was used, in which the pyridyl groups are not coplanar anymore, absorptions from both the Re → bpy and Re → 4,4'-$(CO_2Et)_2$-bpy states were observed in the transient absorbance spectrum of [(bpy)$(CO)_3$Re (3,3'-Me_2-4,4'-bpy)Re$(CO)_3$(4,4'-$(CO_2Et)_2$-bpy)]$^{2+}$.[44,45] Emission maxima and quantum yields were also wavelength dependent and the decay of the transient absorbance and the emission were biexponential with lifetimes of 122 and 263 ns. Apparently, energy transfer is very rapid across 4,4'-bipyridine ($\tau < 10$ ns) but slow in the 3,3'-Me_2-4,4'-bpy bridged complexes on the time scale for decay from the Re → bpy MLCT state. At 77 K the timescales for energy transfer and decay became comparable since residual emission from higher MLCT states was observed.

Guarr and co-workers achieved a similar "fine-tuning" of excited-state energies by using a series of substituted 1,10-phenanthrolines as α-diimine ligand and 4,4'-bpy as a bridge.[46] Emission and transient absorbance spectra were measured for the complex ions $[(L\text{-}L)(CO)_3Re(4,4'\text{-}bpy)Re(CO)_3(L\text{-}L)]^{2+}$ with L-L = 5-Cl-phen, phen, 4-Me-phen, 5,6-Me_2-phen, etc. With the exception of the 5-Cl-phen complex, all binuclear complexes showed the absorptions of the Re → 4,4'-bpy MLCT state in the transient absorbance spectrum. The 5-Cl-phen complex, on the other hand, showed the characteristic emission and absorption of the Re → 5-Cl-phen MLCT state although some population of the Re → 4,4'-bpy MLCT state had also occurred.

Bignozzi, Scandola and co-workers have used for many years the CN^- ion as a bridging ligand since it guarantees a strong electronic coupling and as a result efficient intramolecular energy transfer.[47] Their investigations mainly concerned cyano-bridged adducts of the type $[M\text{-}NC\text{-}Ru(bpy)_2\text{-}CN\text{-}M]^{n+}$. Both linkage isomers $[(phen)(CO)_3Re\text{-}CN\text{-}Ru(bpy)_2\text{-}CN]^+$ and $[(phen)(CO)_3Re\text{-}NC\text{-}Ru(bpy)_2\text{-}CN]^+$ showed the characteristic emission of the $[Ru(bpy)_2]^{2+}$ chromophore, which was monoexponential and independent of excitation wavelength. This means that also for these complexes energy transfer from the Re- to the Ru-fragment is efficient. No emission risetime could be observed which means that the energy transfer process was very fast ($k_{en} > 10^9\ s^{-1}$).

Chromophore–Quencher Complexes

At the end of the seventies the interest shifted more and more from intermolecular to intramolecular light-induced electron transfer. Meyer and co-workers studied the photophysical properties of the complexes $[(MeQ^+)Re(CO)_3(bpy)]^{2+}$ (MeQ^+ = N-methyl-

4,4'-bipyridinium cation) and $[(BzQ^+)Re(CO)_3(bpy)]^{2+}$ (BzQ^+ = N-benzyl-4,4'-bipyridinium cation) between 80 and 295 K.[48] At 80 K in the glass both complexes showed emission from the Re → bpy MLCT state but lifetime and quantum yield decreased dramatically at temperatures above the glass-to-fluid transition ($T >$ 130 K). At the same time a weak new emission appeared at lower energies from the Re → MeQ^+ and Re → BzQ^+ MLCT state, respectively. Absorptions of the $MeQ^\bullet$ radical were observed in the transient absorbance spectrum. These observations were consistent with an intramolecular electron transfer quenching from the Re → bpy MLCT state. The electron transfer product was a lower energy MLCT (Re → Q^+) state which decayed with τ = 52 ns.

$$[(Q^+)Re^I(CO)_3(bpy)]^{2+} \xrightarrow{h\nu} [(Q^+)Re^{II}(CO)_3(bpy^{\bullet -})]^{2+*}, \quad (5)$$

$$[(Q^+)Re^{II}(CO)_3(bpy^{\bullet -})]^{2+*} \rightarrow [(Q^\bullet)Re^{II}(CO)_3(bpy)]^{2+*}, \quad (6)$$

$$[(Q^\bullet)Re^{II}(CO)_3(bpy)]^{2+*} \rightarrow [(Q^+)Re^I(CO)_3(bpy)]^{2+},$$

$$Q^+ = MeQ^+, BzQ^+ \quad (7)$$

The corresponding complex ion $[(MeQ^+)Re(CO)_3(4,4'\text{-}(NH_2)_2\text{-}bpy)]^{2+}$ showed the electron transfer reaction already in the glass.[49] Apparently, intramolecular electron transfer quenching can only occur in such a rigid medium when the driving force for this reaction is large enough. The difference in solvent reorganizational energy between the two MLCT states, $\Delta\lambda_0 = \lambda_{0,2} - \lambda_{0,1}$, must be compensated for by a favourable free energy change $\Delta(\Delta G) = \Delta G_{es,2} - \Delta G_{es,1}$ (see Fig. 10). This explains why for the complexes $[(MeQ^+)Re(CO)_3(4,4'\text{-}(X)_2\text{-}bpy)]^{2+}$ electron transfer quenching was observed in the glass for X = NH_2 ($\Delta(\Delta G) = -1.0$ eV) but not for X = H ($\Delta(\Delta G) = -0.49$ eV) and X = CO_2Et ($\Delta(\Delta G) \cong 0$ eV). The two cases are depicted in Fig. 10, case A being appropriate for X = NH_2, case B for X = H, CO_2Et.

The same effect has recently been observed for these complexes in thin films at room temperature.[50] Again, the $[(MeQ^+)Re(CO)_3\text{-}(4,4'\text{-}(NH_2)_2\text{-}bpy)]^{2+}$ complex showed the absorption of $MeQ^\bullet$ in the transient spectrum, whereas $[(MeQ^+)Re(CO)_3(bpy)]^{2+}$ showed

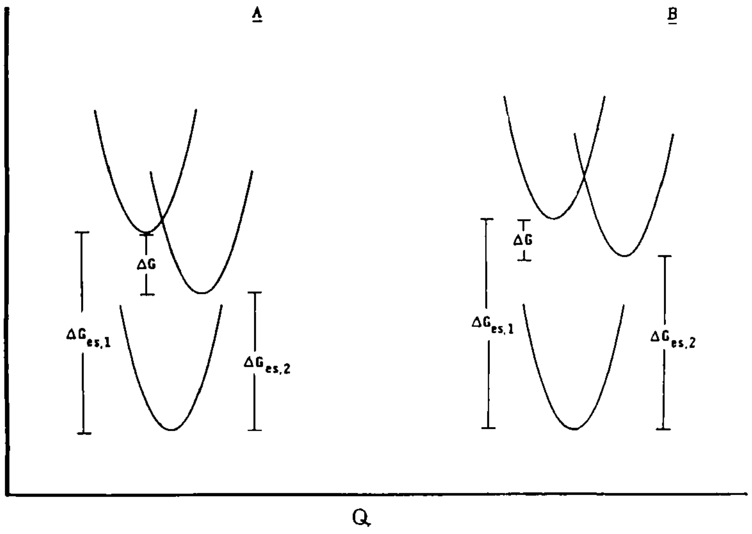


FIGURE 10 Schematic energy–solvent librational coordinate diagrams for light-induced intramolecular electron transfer (from Ref. 49).

the absorption of the Re → bpy MLCT state along with a weak absorption of $MeQ^{\cdot}$. Provided that the driving force is sufficient for electron transfer to take place, polymer matrices have the great advantage over fluid solutions that the lifetime of the charge-separated state is much longer since the frozen dipole orientations cause an increase of the energy gap.

Reductive quenching has been studied for several Re-complexes containing an organic electron donor. Meyer and co-workers studied the complex $[(py\text{-}PTZ)Re(CO)_3(bpy)]^+$, in which py-PTZ represents a pyridine group which is linked at its 4 position to the reducing phenothiazine molecule via a methylene bridge[51,52] (Fig. 11).

Both this complex and the model compound $[(4\text{-}Etpy)Re(CO)_3(bpy)]^+$ showed the same MLCT emission in a glass at 80 K. At room temperature, however, the py-PTZ complex did not emit anymore, whereas the 4-ethylpyridine complex still showed a relatively strong emission. The transient absorbance spectrum of the py-PTZ complex showed a strong absorption of $py\text{-}PTZ^{\cdot +}$ at ~500 nm. Apparently, the MLCT state was quenched by intra-

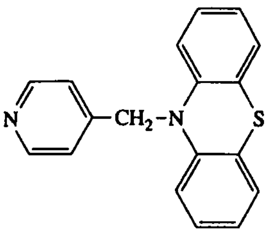


FIGURE 11 Structure of py-PTZ.

molecular electron transfer from py-PTZ to Re^{II} as indicated in the following reactions:

$$[(\text{py-PTZ})\text{Re}^{\text{I}}(\text{CO})_3(\text{bpy})]^+ \xrightarrow{h\nu} \underset{\text{MLCT}}{[(\text{py-PTZ})\text{Re}^{\text{II}}(\text{CO})_3(\text{bpy}^{\bullet -})]^{+*}}, \tag{8}$$

$$[(\text{py-PTZ})\text{Re}^{\text{II}}(\text{CO})_3(\text{bpy}^{\bullet -})]^{+*} \rightarrow \underset{\text{LLCT}}{[(\text{py-PTZ}^{\bullet +})\text{Re}^{\text{I}}(\text{CO})_3(\text{bpy}^{\bullet -})]^{+*}}, \tag{9}$$

$$[(\text{py-PTZ}^{\bullet +})\text{Re}^{\text{I}}(\text{CO})_3(\text{bpy}^{\bullet -})]^{+*} \rightarrow [(\text{py-PTZ})\text{Re}^{\text{I}}(\text{CO})_3(\text{bpy})]^+ . \tag{10}$$

In this way a charge-separated LLCT state was created, which decayed with $\tau = 25$ ns. There was no observable transition from the ground state to the LLCT state, presumably because of negligible electronic coupling between py-PTZ and bpy. The excited state processes involving such LLCT states have recently been reviewed in this journal by Vogler and Kunkely.[53]

These investigations have been extended to a series of complexes $[(\text{py-PTZ})\text{Re}(\text{CO})_3(4,4'\text{-}(\text{X})_2\text{-bpy})]^+$ (X = OCH_3, CH_3, H, C(O)NEt_2, CO_2Et).[54,55] Special attention was paid to the dependence of the rate constant for the back electron transfer reaction (k_{bet}) and $\Delta E_{1/2} = E_{1/2}(\text{py-PTZ}^{+/0}) - E_{1/2}(4,4'\text{-}(\text{X})_2\text{-bpy}^{0/-})$. Values of k_{bet} were determined from the transient absorbance decay curves. The plot of $\ln k_{\text{bet}}$ vs. $\Delta E_{1/2}$ was linear and such linear relationships are predicted by the energy-gap law. The results showed that the energy-gap law is equally applicable to electron transfer in the inverted region.

Similar effects as observed for the oxidative quenching by MeQ^+ in a polymer matrix were observed for the reductive quenching by py-PTZ in the complexes $[(py\text{-}PTZ)Re(CO)_3(4,4'\text{-}(X)_2\text{-}bpy)]^+$. For X = H there was no evidence for quenching of the MLCT emission. The emission was, however, quenched for X = CO_2Et. This result is consistent with the difference in driving force for intramolecular electron transfer from py-PTZ to Re^{II}. Schanze and co-workers used instead 4-(dimethylamino)benzonitrile (DMABN) as electron donor and observed quenching of the emission of $[(DMABN)Re(CO)_3(bpy)]^+$ in CH_3CN but not in CH_2Cl_2.[56] The MLCT and LLCT state of this complex are close in energy and a different solvent polarity changes the driving force for the reaction because of a different influence on $\Delta E_{1/2}$ and E_{MLCT} ($\Delta G \cong \Delta E_{1/2} - E_{MLCT}$).

For a series of complexes containing different α-diimine ligands and a dimethylaniline as electron donor, rates for forward electron transfer (k_{fet}, MLCT → LLCT) and back electron transfer (k_{bet}, LLCT → ground state) were determined from time-resolved emission and absorption spectra, respectively.[57] Values of k_{fet} increased as ΔG_{et} became more exothermic. However, contrary to the observations of Meyer *et al.*,[55] a weakly inverted dependence of k_{bet} on free energy charge was observed.

Schanze and co-workers also used for the first time an organic ligand with a cyclohexyl group as rigid spacer between the electron donor and the transition metal.[58] Again, rapid intramolecular electron transfer was observed.

Metal–Metal Bonded Complexes, a Special Case of Chromophore–Quencher Complexes?

A special group of Re-α-diimine complexes are the metal–metal bonded compounds $[L_nMRe(CO)_3(L\text{-}L)]$ in which L_nM represents a metal fragment such as $(CO)_5Mn$, $(CO)_5Re$, $(CO)_4Co$, Ph_3Sn, etc. (Fig. 12).

Wrighton and co-workers studied in detail the absorption and emission spectra, and the photochemistry of several of these complexes, viz. $[L_nMRe(CO)_3(L\text{-}L)]$ (L_nM = $(CO)_5Mn$, $(CO)_5Re$,

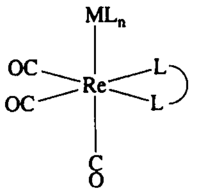
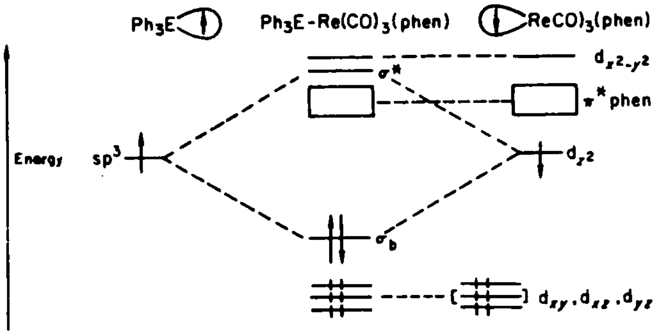


FIGURE 12 Structure of the complexes $[L_nMRe(CO)_3(L\text{-}L)]$.



SCHEME I One-electron diagram for $[(Ph_3E)Re(CO)_3(phen)]$ (E = Ge, Sn) (from Ref. 61).

Ph_3Sn, Me_3Sn, Ph_3Ge or Me_3Ge; L-L = phen, bpy or 2,2′-biquinoline).[59–61] Taking into account the low ionization potential (IP) of the electrons in the metal–metal bonding orbital (σ_b) of $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$ and $Me_3SnMn(CO)_5$, the authors proposed the m.o. diagram for these complexes, presented in Scheme I. The low IP of σ_b in these complexes was confirmed by the UV-PES data of the complexes $[(CO)_5MRe(CO)_3(L\text{-}L)]$ (M = Mn,Re; L-L = iPr-DAB).[62] These spectra showed that σ_b(M-Re) is the h.o.m.o. of most of these complexes and that it is close in energy to the d_π(Re) orbitals of the $Re(CO)_3$(L-L) fragment. Moreover, the first oxidation potential and the products formed upon oxidation depended on the L_nM fragment.[61] Since the l.u.m.o. is the lowest π^*-orbital of L-L, the first absorption band of these complexes (450–650 nm) was assigned to the $\sigma_b(M\text{-}Re) \rightarrow \pi^*(L\text{-}L)$ transition. This assignment was consistent with the solvatochromism of the absorption band and with the dependence of its position on L-L and on the metal fragment L_nM.

The metal–metal bonded complexes [$L_nMRe(CO)_3$(L-L)] are all very photosensitive, giving rise to homolysis of the M-Re bond. At the same time several of these complexes showed emission at room temperature in fluid solution.[60,61] The photochemical quantum yields as well as the emission spectra, lifetimes and quantum yields were wavelength independent and both the reaction and emission were quenched by anthracene giving rise to the same quenching constant in a Stern–Volmer plot. From these observations it was concluded that emission and homolysis reaction resulted from the same lowest $^3\sigma_b\pi^*$ excited state. More recent UV/Vis and resonance Raman studies showed, however, that the assignment of the lowest-energy absorption band to a single $\sigma_b \rightarrow \pi^*$ transition cannot be correct.[63–65] For, the band consists of more than one electronic transition since it becomes highly structured upon cooling to a glass at 77 K. Similar structured bands have been observed for mononuclear α-diimine complexes such as [$ClRe(CO)_3$(L-L)],[9] [$M(CO)_4$(L-L)] (M = Cr,Mo,W),[66–68] [$Fe(CO)_3$(L-L)][69] and [$Ni(CO)_2$(L-L)][70] and their intensities and solvatochromism are also very much alike. Just as for these mononuclear complexes, the first absorption band of the metal–metal bonded complexes must therefore, at least in part, belong to d_π(Re) → π^*(L-L) MLCT transitions. This conclusion was confirmed by the resonance Raman (rR) spectra of the complexes [$(CO)_5MRe(CO)_3$(iPr-DAB)] (M = Mn,Re) dissolved in an N_2 matrix at 10 K.[64] These spectra showed that the charge transfer character of the main electronic transition of the first absorption band decreased appreciably going from [$(CO)_5MnRe(CO)_3$(iPr-DAB)] to [$(CO)_5ReRe(CO)_3$(iPr-DAB)]. This behaviour, also observed for several of the mononuclear α-diimine complexes, is a typical property of MLCT transitions between metal-d_π and ligand-π^* orbitals of the same symmetry. The extent of mixing between such orbitals (π-backbonding in the ground state) will directly influence the MLCT character of the electronic transition between them. In the limit of complete mixing the d_π(Re) → π^*(L-L) transition will lose its MLCT character and become a metal–ligand bonding to antibonding transition $(d_\pi + \pi^*) \rightarrow (\pi^* - d_\pi)$. Such a situation had nearly been reached for the complex [$(CO)_5ReRe(CO)_3$(iPr-DAB)]. The rR spectra of these complexes did also show no rR effect for the metal–metal stretching mode ν_s(M-Re), again arguing against the presence of a strongly absorbing $\sigma_b \rightarrow \pi^*$ transition.

Based on these observations the lowest-energy absorption band has been reassigned to a superposition of MLCT transitions within the $Re(CO)_3$(L-L)-moiety.[64] The $\sigma_b \rightarrow \pi^*$ transition may also be within this band, but it cannot be a major contributor to its intensity. In accordance with this assignment, Larson, Oskam and Zink assigned the low-energy emission of the complexes $[(CO)_5ReRe(CO)_3(L\text{-}L)]$ (L-L = bpy, 4,4′-Me_2-bpy, phen, iPr-PyCa, iPr-DAB, or pTol-DAB) to phosphorescence from a ^{3}MLCT state.[65] For some of the complexes they observed at 20 K a weak, short-lived ^{1}MLCT fluorescence at the high-energy side of the phosphorescence.

Occupation of an MLCT state by low-energy excitation will not give rise to the efficient homolysis reaction of these $[L_nMRe(CO)_3(L\text{-}L)]$ complexes. The high quantum yields of this reaction and their temperature and wavelength independence can only be explained with a fast crossing to a reactive state of the complexes. This state may be either the $^3\sigma_b\pi^*$ state proposed by Wrighton and co-workers, or the $^3\sigma_b\sigma^*$ state of the metal–metal bond. The repulsive $^3\sigma_b\sigma^*$ state is responsible for the homolysis reaction of the parent complexes $M_2(CO)_{10}$ (M = Mn,Re) and crossing to this state has therefore been presented as an alternative explanation for the homolysis reaction by Meyer and Caspar.[71] In order to decide which interpretation is preferred, we have to consider that the photochemical quantum yield is temperature and wavelength independent and that the quenching constant is the same for reaction and emission.[60] This can only be the case when the two states involved in emission and photochemistry, respectively, have very similar electron configurations so that the crossing between the states is very fast. In this respect the $^3\sigma_b\pi^*$ state is a much better candidate than $^3\sigma_b\sigma^*$ since surface crossing from a $^3d_\pi\pi^*$ (MLCT) state to $^3\sigma_b\pi^*$ only involves intramolecular electron transfer from σ_b to d_π. On the other hand, the electronic configurations of the $^3d_\pi\pi^*$ and $^3\sigma_b\sigma^*$ states are so different that crossing between these states is expected to be slow.

It is therefore tentatively concluded that mainly MLCT states are involved in absorption and emission of these complexes and that the reaction takes place from a close-lying $^3\sigma_b\pi^*$ state. In this respect, there seems to be a close analogy with the chromophore–quencher complexes discussed in the preceding section. In both cases irradiation leads to population of an MLCT state. The chromophore–quencher complexes then undergo fast intramolecular electron transfer from the organic donor to the metal to give an LLCT state which decays to the ground state. In the metal–metal bonded complexes population of the MLCT state is followed by electron transfer from the metal–metal bond to Re. The "LLCT" state $^3\sigma_b\pi^*$ thus formed does, however, not decay to the ground state but gives rise to the homolysis reaction. For both types of complexes there is no observable transition from the ground state to the LLCT state.

In recent years we have studied the photochemistry of a series of metal–metal bonded complexes $[L_nMM'(CO)_3(L\text{-}L)]$ (L_nM = $(CO)_5Mn$, $(CO)_5Re$, $(CO)_4Co$, $Cp(CO)_2Fe$, Ph_3Sn; M' = Mn,Re) and mainly focused on the stoichiometric and catalytic reactions of the radicals formed upon irradiation.[72,73] Most Re-complexes showed the same wavelength and temperature independent homolysis reaction as observed by Wrighton and co-workers. However, one Re-complex appeared to be photostable at 0°C. This is the trinuclear complex $[(CO)_5MnRe\ (CO)_3(bpm)Re(CO)_3Br]$ (bpm = 2,2'-bipyrimidine) in which two Re atoms are bonded to the bridging bpm ligand.[74] The complex has low-energy MLCT transitions (λ_{max} = 665 nm) to bpm. At 0°C the complex is photostable; at 25°C homolysis of the Mn-Re bond occurs with a quantum yield of ca. 0.1. The corresponding binuclear complex $[(CO)_5MnRe(CO)_3(bpm)]$ (λ_{max} = 520 nm) showed the normal efficient homolysis reaction at 0°C. This result shows that in the trinuclear complex the energy of the MLCT state is lower than the dissociation energy of the metal–metal bond. Cleavage of this bond can only be achieved by raising the temperature or by exciting at shorter wavelength.

More and more, these light-induced homolysis reactions appear to be a general property of complexes having a lowest MLCT state and a homopolar metal–ligand or metal–metal bond. In some cases the LLCT state is populated directly by excitation; in most complexes, however, the reactive LLCT state is occupied indirectly after irradiation into an MLCT transition. The complexes $[R_2Zn(L\text{-}L)]$ (R = alkyl) possess such an intense LLCT transition from the antisymmetric Zn-R σ-bond combination to the lowest π^* orbital of the α-diimine ligand.[53,75] Irradiation into this transition leads to homolysis of a Zn-R bond and to interesting thermal reactions of the radicals formed.[75] The complexes $[RRu(CO)_3X(L\text{-}L)]$ (X = halide) are photostable for R = Me and benzyl, but photodecompose for R = iPr.[76] At the same time, the $\sigma_b(Ru\text{-}R) \rightarrow \pi^*(L\text{-}L)$ (LLCT) transition shifts to lower energy and nearly coincides with the $d_\pi(Ru) \rightarrow \pi^*(L\text{-}L)$ (MLCT) transitions for R = iPr. For the corresponding $[RRe(CO)_3(L\text{-}L)]$ complexes no separate LLCT transition is observed, yet they photodecompose into radicals just as the metal–metal bonded complexes $[L_nMRe(CO)_3(L\text{-}L)]$.[77]

CONCLUSION

The complexes $[(L)Re(CO)_3(L\text{-}L)]^{o/+}$ have been shown to be excellent model systems to study the properties of MLCT states. The factors that influence the lifetimes of these states have been determined. Energy and electron transfer processes and photoreactions could be observed by making a good choice of L and L-L.

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