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The photochemistry of (CO)5MnMn(CO)3(α-diimine) and XMn(CO3)(α-diimine) (X=halide) complexes

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Abstract

The $Mn(CO)_5$ and $Mn(CO)_3$(α-diimine) radicals formed by irradiation of a $(CO)_5MnMn(CO)_3$(α-diimine) complex undergo interesting radical coupling and electron transfer (chain) reactions. The mechanisms of these reactions are discussed and attention is paid to the character of the reactive excited state.

A relationship is proposed to exist with the corresponding halide complexes $XMn(CO)_3$(α-diimine) (X=Cl,Br,I) which similarly undergo homolysis of the Mn-X bond upon irradiation. Preliminary m.o. data of $XMn(CO)_3$(bpy) and resonance Raman results obtained for $BrRe(CO)_3$(pTol-DAB) confirm the presence of a lowest LLCT state at least for the halide complexes.

1. INTRODUCTION

Most complexes containing an α-diimine ligand such as 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) are characterized by intense absorption bands in the visible or near ultraviolet. For complexes of low valent transition metals these bands belong to metal to ligand charge transfer (MLCT) transitions directed to the lowest π* orbital of the α-diimine. The spectroscopy, photophysics and photochemistry of such complexes has recently received wide interest because they can often act as efficient photosensitizers for intra- and intermolecular energy and electron transfer processes (e.g. $Ru(bpy)_3^{2+}$) [1]. Our work in this field has concerned the spectroscopy and photochemistry of a series of complexes of the type $M(CO)_4$(α-diimine) (M=Cr,Mo,W), $M'(CO)_3$(α -diimine) (M'=Fe,Ru), $Ni(CO)_2$(α-diimine) and $L'_nM'M(CO)_3$(α-diimine) (M=Mn,Re; $L'_nM'=(CO)_5Mn$, $(CO)_5Re$, $(CO)_4Co$, $Cp(CO)_2Fe$, Ph_3Sn). The results of these studies have recently been reviewed [2]. Due to the presence of a metal-metal bond the complexes $L'_nM'M(CO)_3$(α -diimine) are much more photolabile than the corresponding mononuclear α-diimine complexes. In most cases the metal-metal bond is split homolytically with formation of $M'L'_n$ and $M(CO)_3$(α-diimine) radicals. Different mechanisms have been proposed for these photoreactions. Wrighton and coworkers, who first studied the photophysics and photochemistry of the complexes $(CO)_5MRe(CO)_3$(phen) (M=Mn,Re), ascribed the photolability to population of the $^3\sigma\pi^*$ state by irradiation into the allowed transition from the σ-orbital of the metal-metal bond to the lowest π* orbital of the α-diimine [3]. This mechanism is closely related to that of the complexes ZnR_2(α-diimine) which produce ·R and ZnR(α-diimine·) radicals upon irradiation into their σ(Zn-R) to π*(α-diimine) (LLCT) transition [4]. An alternative mechanism, first proposed by Meyer and Caspar, involves a surface crossing from (a) non-reactive MLCT state(s) to the repulsive $^3\sigma\sigma^*$ state of the metal-metal bond [5]. A similar mechanism has e.g. been proposed for the splitting of the metal-alkyl bond of the alkylmetallo-porphyrins upon irradiation into their $\pi \rightarrow \pi^*$ transitions [6].

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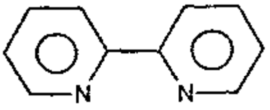
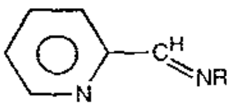
In the course of our photochemical studies on these $L'_nM'M(CO)_3$(α-diimine) complexes we have adopted the model proposed by Meyer and Caspar since the visible absorption bands of these complexes have the characteristic features (solvatochromism, intensity, resonance Raman effects) of MLCT transitions [7]. The two-level scheme proposed by Meyer and Caspar has, however, become questionable since the quantum yields of the photochemical reactions of these complexes appeared to be wavelength and temperature independent [8]. Moreover, a close analogy has recently been found between the photochemistry of the complexes $(CO)_5MnMn(CO)_3$(α-diimine) and of the corresponding halides $XMn(CO)_3$(α-diimine). The latter complexes are characterized by a lowest X→α-diimine (LLCT) state.

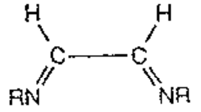
We here report and discuss the photochemistry of a representative series of complexes, $(CO)_5MnMn(CO)_3$(α-diimine), and the preliminary photochemical data of the corresponding halides $XMn(CO)_3$(α-diimine) (X=Cl,Br,I). The general structures of the α-diimine ligands used are:



2,2'-bipyridine
(bpy)



pyridine-2-carbaldehyde imine
(R-PyCa)



1,4-diaza-1,3-butadiene
(R-DAB)

2. RESULTS AND DISCUSSION

The absorption spectra of the $(CO)_5MnMn(CO)_3$(α-diimine) complexes show two strong absorption bands, at ca. 350 and 550 nm respectively. The high energy band belonging to the $\sigma \rightarrow \sigma^*$ transition of the Mn-Mn bond, is close in energy to the corresponding transition of $Mn_2(CO)_{10}$. The intense ($\varepsilon = (5\text{-}12) \times 10^3 M^{-1}cm^{-1}$) band in the visible region has been assigned to $d_\pi(Mn) \rightarrow \pi^*$(α-diimine) MLCT transitions because of its intensity, solvatochromic behaviour and the results of resonance Raman (rR) measurements. However, although the rR spectra do not provide evidence for an underlying $\sigma \rightarrow \pi^*$ (LLCT) transition, such a transition will certainly be close in energy to the MLCT transitions since the σ and $d_\pi(Mn)$ orbitals nearly coincide [9].

2.1 Photochemistry of $(CO)_5MnMn(CO)_3$(α-diimine)

The photochemistry of several of these complexes has been studied in different media at temperatures ranging from 133 K to room temperature, both in the absence and presence of radical scavengers or Lewis bases. Intermediates were identified with IR, UV/Vis, or ESR spectroscopy and several photoproducts were structurally characterized by an X-ray structure determination.

Photolysis in viscous and non-viscous solvents

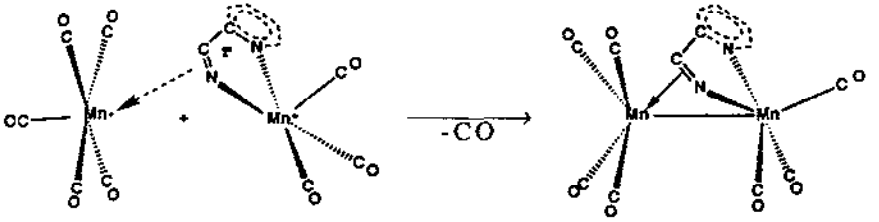
Although irradiation into the visible absorption band leads to both homolysis of the metal-metal bond and release of CO, only the first reaction gives rise to the formation of stable photoproducts, according to reactions 1-3.

$$(CO)_5MnMn(CO)_3(\alpha\text{-diimine}) \xrightarrow{h\nu} Mn(CO)_5 + Mn(CO)_3(\alpha\text{-diimine}) \quad (1)$$

$$2\ Mn(CO)_5 \longrightarrow Mn_2(CO)_{10} \quad (2)$$

$$2\ Mn(CO)_3(\alpha\text{-diimine}) \rightleftarrows Mn_2(CO)_6(\alpha\text{-diimine})_2 \quad (3)$$

According to the ESR spectra the $Mn(CO)_3^{\cdot}$(α-diimine) radicals formed are 16e-species with the unpaired electron in the lowest π* orbital of the α-diimine ligand. The energy of this orbital and the steric interaction between the α-diimines in the dimer, determine the position of the equilibrium of reaction (3). Reactions (2) and (3) will of course be inhibited in viscous solvents such as paraffin. The radicals can then not diffuse from the solvent cage. They will react back with each other to give the parent complex. In case of the R-PyCa and R-DAB complexes this backreaction leads, however, to the formation of new complexes $(CO)_4Mn(\sigma,\sigma,\eta^2$-R-PyCa)$Mn(CO)_3$ and $(CO)_3Mn(\sigma,\sigma,\eta^4$-R-DAB)$Mn(CO)_3$ respectively, in which the R-PyCa (R-DAB) ligand is now σ,σ-coordinated to one metal and $\eta^2(\eta^4)$ to the other [8]. Since the reaction is quenched by radical scavengers these products are not formed by release of CO but after homolysis of the metal-metal bond. One has to realize that a simple backreaction of the radicals via coupling of the Mn atoms cannot take place here since the unpaired electron of the $Mn(CO)_3$(α-diimine) radical resides on the α-diimine ligand. The radical coupling will therefore take place between the radical anion of $^+Mn(CO)_3$(α-diimine$^-$) and the Mn atom of $Mn(CO)_5$. This reaction (4) then leads to the formation of ligand bridged complexes.



(4)

An interesting photoreaction has been observed for the complexes $(CO)_5MnRe(CO)_3(bpy')$ (bpy'=4,4'-dimethyl-2,2'-bipyridine) [10] and $(CO)_4CoRe(CO)_3$-(bpy) [11] in toluene at T≤230 K. Irradiation in this viscous medium gives rise to the formation of the contact ion pairs $[Mn(CO)_5^-$---$Re(CO)_3(bpy')^+]$ and $[Co(CO)_4^-$---$Re(CO)_3(bpy)^+]$, respectively. In this case the radical anion of the $^+Re(CO)_3(bpy^-)$ radical transfers an electron to the $Mn(CO)_5$ or $Co(CO)_4$ radical. The ions thus formed cannot react back at these low temperatures to give the thermodynamically more stable starting complexes since a CO-group of the $Mn(CO)_5^-$ or $Co(CO)_4^-$ anion is bonded to the Re atom of the coordinatively unsaturated cation. Raising the temperature causes the breaking of this bond and back electron transfer to give the parent metal-metal bonded complex.

Electron transfer reactions in the presence of Lewis bases

The observation of electron transfer reactions in non-coordinating solvents such as toluene depends on the formation of stable contact ion pairs. Otherwise, the ions formed will readily react with each other to give the parent complex.

In the presence of a Lewis base, on the other hand, electron transfer between the radicals normally leads to the formation of stable ions. Thus, irradiation of a solution of a $(CO)_5MnMn(CO)_3$(α-diimine) complex in 2-MeTHF at 180 K produces $Mn(CO)_3$(α-diimine)-(2-MeTHF)$^+$ and $Mn(CO)_5^-$ [10].The 16e-$Mn(CO)_3$(α-diimine) radicals formed by homolysis of the Mn-Mn bond, easily take up a solvent molecule and the 18e-$Mn(CO)_3$(α-diimine)(2-MeTHF) adducts thus formed reduce the $Mn(CO)_5$ radicals. The backreaction of the $Mn(CO)_3$(α-diimine)(2-MeTHF)$^+$ and $Mn(CO)_5^-$ ions is prevented here by the coordinated solvent molecules. Raising the temperature causes these molecules to be released and the ions to react back to give the starting complex. Every Lewis base can in fact form such an adduct but its thermal stability strongly depends on the bulkiness and basic properties of the base. At room temperature hard bases such as 2-MeTHF or THF coordinate only weakly because of the strongly electron donating properties of the α-diimine^{-} radical anion.

Soft bases such as PR_3 not only form more stable adducts $Mn(CO)_3(\alpha\text{-diimine})(PR_3)$ at room temperature, their photodisproportionation reaction is even catalytic with quantum yields as high as 100. We are dealing here with an electron transfer chain (e.t.c.) reaction, in which the highly reducing adduct $Mn(CO)_3(\alpha\text{-diimine})(PR_3)$ reduces the parent complex [12]. The reduced complex decomposes into $Mn(CO)_5^-$ and a new $Mn(CO)_3(\alpha\text{-diimine})$ radical which starts the catalytic cycle. These reactions are summarized in eq 5-10 ($P=PR_3$).

Reaction

$$(CO)_5MnMn(CO)_3(\alpha\text{-diimine}) + P \xrightarrow[\phi>1]{h\nu} Mn(CO)_3(\alpha\text{-diimine})P^+ + Mn(CO)_5^- \tag{5}$$

Initiation

$$(CO)_5MnMn(CO)_3(\alpha\text{-diimine}) \xrightarrow{h\nu} Mn(CO)_5 + Mn(CO)_3(\alpha\text{-diimine}) \tag{6}$$

Propagation

$$Mn(CO)_3(\alpha\text{-diimine}) + P \longrightarrow Mn(CO)_3(\alpha\text{-diimine})P \tag{7}$$

$$\begin{aligned} Mn(CO)_3(\alpha\text{-diimine})P + (CO)_5MnMn(CO)_3(\alpha\text{-diimine}) \longrightarrow {} & Mn(CO)_3(\alpha\text{-diimine})P^+ + \\ & + Mn(CO)_5^- + Mn(CO)_3(\alpha\text{-diimine}) \end{aligned} \tag{8}$$

Termination

$$Mn(CO)_3(\alpha\text{-diimine})P + Mn(CO)_5 \longrightarrow Mn(CO)_3(\alpha\text{-diimine})P^+ + Mn(CO)_5^- \tag{9}$$

$$2Mn(CO)_3(\alpha\text{-diimine}) \longrightarrow Mn_2(CO)_6(\alpha\text{-diimine})_2 \tag{10}$$

The $Mn(CO)_3(\alpha\text{-diimine})(PR_3)$ radicals cannot only initiate the catalytic disproportionation of their metal-metal bonded precursors, they can also catalyze substitution reactions of organometallic complexes. A good example is the substitution of CO in $Ru_3(CO)_{12}$ by PR_3, a reaction which starts to proceed very fast if a small amount of a $(CO)_5MnMn(CO)_3(\alpha\text{-diimine})$ complex is added to the solution [12]. The mechanism of this reaction is presented in eq. 11-16 ($P=PR_3$).

Reaction

$$Ru_3(CO)_{12} + P \longrightarrow Ru_3(CO)_{11}P + CO \tag{11}$$

Initiation

$$(CO)_5MnMn(CO)_3(\alpha\text{-diimine}) \xrightarrow{h\nu} Mn(CO)_5 + Mn(CO)_3(\alpha\text{-diimine}) \tag{12}$$

$$Mn(CO)_3(\alpha\text{-diimine}) + P \longrightarrow Mn(CO)_3(\alpha\text{-diimine})P \tag{13}$$

$$Mn(CO)_3(\alpha\text{-diimine})P + Ru_3(CO)_{12} \longrightarrow Mn(CO)_3(\alpha\text{-diimine})P^+ + Ru_3(CO)_{12}^- \tag{14}$$

Propagation

$$Ru_3(CO)_{12}^- + P \longrightarrow Ru_3(CO)_{11}P^- + CO \tag{15}$$

$$Ru_3(CO)_{11}P^- + Ru_3(CO)_{12}^- \longrightarrow Ru_3(CO)_{11}P + Ru_3(CO)_{12}^- \tag{16}$$

The mechanisms of the above catalytic processes are similar to those initiated by the 19e-radicals $CpMo(CO)_3(PR_3)$ [13], $CpFe(CO)_2(PR_3)$ [14], $W(CO)_5(L)^{\cdot}$ [15], and $Mn(CO)_3(N)_3$ [16]. The electron transfer reactions of these latter radicals, including the catalyzed substitution of CO in $Ru_3(CO)_{12}$ by PR_3, have been described and reviewed by Tyler [17]. Because of their 19-electron configuration these metal centred radicals are better reducing agents than the ligand localized 18e-$Mn(CO)_3(\alpha\text{-diimine})(PR_3)$ radicals. These latter species have, however, the advantage that they can easily be prepared in high yield in diffuse daylight without using an irradiation source.

The reducing power of the $Mn(CO)_3$(α-diimine)(PR_3) radicals is mainly determined by the reduction potential of the coordinated α-diimine ligand and to a much lesser extent by the basicity of the PR_3 ligand [12].

The necessity to stabilize the $Mn(CO)_3$(α-diimine) radicals by a soft base such as a PR_3 ligand for these e.t.c. reactions, is a real disadvantage. For such a reactive ligand may start undesired sidereactions. In order to avoid the use of these ligands we have recently started an investigation into the intramolecular stabilization of the radicals. For this purpose we have synthesized several tridentate α-diimine ligands which coordinate as a chelate in the $(CO)_5MnRe(CO)_3$(α-diimine) complex but bind to the metal via all three N-atoms in the $Re(CO)_3$(α-diimine) radical. According to the ESR spectra photolysis of such metal-metal bonded complexes produces indeed 18e-$Re(CO)_3$(α-diimine) radicals with the radical anion acting as a tridentate ligand. The third metal-nitrogen bond is, however, very weak and can easily be broken by a PR_3 ligand. We are therefore now synthesizing a complex of a substituted phenanthroline ligand having a sidearm with a P-donor atom.

2.2 Photochemistry of $XMn(CO)_3(bpy)$ (X=Cl,Br,I)

Although the $XRe(CO)_3(bpy)$ (X=halide) complexes have been studied in detail [18], hardly any attention has been paid to the photochemical behaviour of the corresponding $XMn(CO)_3(bpy)$ complexes. This is the more surprizing since these complexes show an interesting LLCT photochemistry not observed for the corresponding Re-complexes. Irradiation of $XMn(CO)_3(bpy)$ into the visible absorption band produces $Mn_2(CO)_6(bpy)_2$. The reaction takes place for X=Cl,Br and I. The formation of this photoproduct points to a reaction from an X^- to bpy LLCT state and in order to rationalize this tentative conclusion we have undertaken a m.o. calculation of $XMn(CO)_3(bpy)$ (X=Cl,Br). The preliminary results of these calculations show that the h.o.m.o. has mixed metal and halide but mainly $X^-(p_\pi)$ character. There is an increasing anti-bonding interaction between the $X^-(p_\pi)$ and $Mn(d_\pi)$ orbitals going from I^- to Cl^-. The l.u.m.o. is the bpy(π^*_1) orbital and the lowest-energy transition is therefore $X^- \rightarrow$bpy (LLCT). The first MLCT transition of these complexes is expected at somewhat higher energy.

Irradiation into the LLCT transition is not expected to weaken the Mn-X bond because of the anti-bonding interaction in the h.o.m.o. Maybe that the large charge shift during this transition is responsible for the observed loss of X.

In order to prove the LLCT character of the lowest-energy transition we have tried to measure the resonance Raman (rR) spectra of $BrMn(CO)_3(bpy)$. These attempts failed because of the photolability of the complex. RR spectra were therefore measured for the photostable $BrRe(CO)_3(bpy)$ complex. These spectra did also not provide clear evidence about the presence of a LLCT transition due to disturbing luminescence. However, by using instead pTol-DAB as an α-diimine, a LLCT transition could be detected in the absorption spectra and identified with rR spectroscopy. The absorption spectra of $XRe(CO)_3$(pTol-DAB) showed the presence of a strong absorption band at ca. 400 nm and a weaker one at ca. 500 nm. The latter band was not present in the spectrum of the corresponding (OTF)$Re(CO)_3$(pTol-DAB) (OTF=trifluoromethylsulfonate). The rR spectra obtained by excitation into the 500 nm shoulder showed resonance enhancement of Raman intensity for ν(Re-X) and for symmetric stretching modes of the pTol-DAB ligand. These rR effects agree with an assignment of this band to an X→pTol-DAB (LLCT) transition.

When the wavelength of the exciting laser line was shifted to shorter wavelength, the Raman band belonging to ν(Re-X) disappeared and a ν(CO) band showed up next to the bands of the pTol-DAB vibrations. These latter rR effects are typical for excitation into an MLCT transition [2]. These results show that the complexes $XRe(CO)_3$(pTol-DAB) have close-lying LLCT and MLCT transitions. The same will hold for the corresponding $XRe(CO)_3(bpy)$ complexes but this is not evident from the absorption and rR spectra. Apparently, the MLCT and LLCT transitions of these latter complexes coincide. Replacing bpy by pTol-DAB will cause a shift of the MLCT transitions to higher energy with respect to the LLCT transition because of an increase in metal to pTol-DAB π-backbonding. These results support the LLCT assignment for the lowest excited state of the corresponding $XMn(CO)_3$(α-diimine) complexes.

It does, however, not explain the large difference in photoreactivity between the Mn and Re complexes. The presence of a low-lying LLCT state has also consequences for a correct interpretation of the excited state properties of the Re-complexes. Both aspects are the subject of further investigations.

3. SUMMARY

The complexes $(CO)_5MnMn(CO)_3(\alpha\text{-diimine})$ and $XMn(CO)_3(\alpha\text{-diimine})$ show a striking similarity in their photochemical behaviour since they both produce the dimeric species $Mn_2(CO)_6(\alpha\text{-diimine})_2$ upon irradiation into their lowest-energy absorption band. It is therefore tempting to propose a reactive LLCT state for both types of complexes although the characters of their h.o.m.o.'s will of course be different.

As mentioned in the Introduction the temperature and wavelength independence of the quantum yields does not support a two-level scheme for the metal-metal bonded complexes involving a non-reactive MLCT state and the reactive $^3\sigma\sigma^*$ state of the metal-metal bond. Definite proof for a one-level scheme involving a reactive LLCT state is, however, still lacking for these complexes. Picosecond flash photolysis has already shown that the primary photoproduct is formed within 20 ps. However, only femtosecond flash photolysis can provide convincing evidence for such a one-level scheme and such experiments are planned for the near future.

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