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The photochemical formation of organometallic radicals from α-diimine complexes having a metal-metal, metal-alkyl or metal-halide bond.

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ABSTRACT

This article describes the homolytic splitting of metal-metal, metal-alkyl and metal-halide bonds by visible excitation of α-diimine complexes into their MLCT transitions. It is shown that mechanistic information about these reactions can best be obtained from the alkyl complexes which show a strong dependence of their quantum yield on the alkyl group. A detailed mechanism is presented for the photochemistry of *fac*-XMn(CO)$_3$(α-diimine)(X= halide) which complexes, quite unexpectedly, photodecompose into radicals Mn$^+$(CO)$_3$(α-diimine$^{\cdot -}$) via their *mer*-isomers.

A. INTRODUCTION

The metal-metal bonded complexes L$_n$MM'(CO)$_3$(α-diimine) (L$_n$M=(CO)$_5$Mn, (CO)$_5$Re, (CO)$_4$Co, Ph$_3$Sn, etc.; M'=Mn,Re) [1-3] and the alkyl complexes R$_2$Zn(R'-DAB) [4], RM(porphyrin) (M=Al,Ga,In) [5-7] and the alkylcobalamins [8-10] have in common that they undergo homolysis of the metal-metal or metal-alkyl bond upon visible excitation. In the case of R$_2$Zn(R'-DAB) the reactive state has $\sigma_b\pi^*$ character since σ_b(Zn-R)$\rightarrow\pi^*$(R'-DAB) is the only low-energy transition of these complexes. The situation is less clear for the other complexes since the $\sigma_b\rightarrow\pi^*$ transition can only be a minor contributor to their visible absorption bands which belong to $d_\pi\rightarrow\pi^*$(MLCT) or $\pi\rightarrow\pi^*$ (IL) transitions. Since the MLCT and IL states themselves are not reactive, the homolysis reaction has been explained with a surface crossing to a reactive $^3\sigma_b\pi^*$ or $^3\sigma_b\sigma^*$ state [1,6,10-12]. The first mechanism relates to the behaviour of the Zn-complexes, the second one to the photochemistry of parent complexes such as M$_2$(CO)$_{10}$ (M=Mn,Re) and RRe(CO)$_5$.

In this article we present evidence for a reactive $^3\sigma_b\pi^*$ state in the case of the alkyl complexes RRe(CO)$_3$(α-diimine) [13]. It is also shown that even for the complexes *mer*-XMn(CO)$_3$(bpy) (X=halide) visible excitation leads to homolysis of the Mn-halide bond and that excitation of Os$_3$(CO)$_{10}$(α-diimine) gives rise to cleavage of a metal-metal bond followed by complete recovery of the metal cluster. The general structures of the α-diimine ligands used are shown in Fig. 1.

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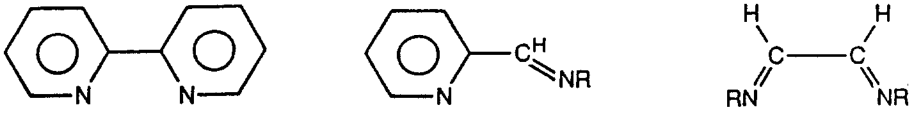


2,2'-bipyridine (bpy) pyridine-2-carbaldehyde imine (R-PyCa) 1,4-diaza-1,3-butadiene (R-DAB)

Fig. 1 Structures of the α-diimine ligands used.

B. RESULTS AND DISCUSSION

(i) Metal-metal bonded complexes

The complexes $L_nMM'(CO)_3$(α-diimine)($L_nM=(CO)_5Mn$, $(CO)_5Re$, $(CO)_4Co$, Ph_3Sn etc.; M'=Mn,Re) are characterized by strong absorption bands between 500 and 600 nm which have been assigned to MLCT transitions within the $M'(CO)_3$(α-diimine) fragment [1-3,11,14]. For M'=Re the complexes undergo homolysis of the M-M' bond with quantum yields higher than 0.1, which are temperature and wavelength independent. In view of the absence of an allowed $\sigma_b(M\text{-}M') \rightarrow \pi^*$(α-diimine) transition in the visible, this homolysis reaction most likely occurs from the $^3\sigma_b\pi^*$ state after surface crossing from the MLCT states. The temperature and wavelength independence of the quantum yields places the reactive $^3\sigma_b\pi^*$ state at lower energy than the MLCT states in agreement with the UV-Photoelectron spectra. These spectra showed that the $\sigma_b(M\text{-}M')$ orbital has a lower Ionization Potential than the $d_\pi(M')$ orbitals responsible for the MLCT transitions [15].

For M'=Mn, the photochemistry is more complicated since these complexes can also undergo release of CO from the lowest LF state of the $Mn(CO)_3$(α-diimine) fragment. There appeared to be a competition between homolysis of the M-Mn bond and release of CO which is most probably determined by the relative energies of the reactive $\sigma_b\pi^*$ and dd* states. Thus, the complexes $L_nMMn(CO)_3$(α-diimine) ($L_nM=(CO)_5Re$, Ph_3Sn) having a strong metal-metal bond, only showed release of CO, the complexes $(CO)_5MnMn(CO)_3$(α-diimine) underwent both reactions , and the complexes $(CO)_4CoMn(CO)_3$(α-diimine) only photodecomposed into radicals. A similar competition has recently been observed by us for the corresponding alkyl complexes $RMn(CO)_3$(α-diimine) which showed release of CO for R=Me and homolysis of the Mn-R bond for R=benzyl [16]. The radicals formed by the homolysis reactions showed interesting radical coupling and electron transfer chain reactions which have been studied in detail [17,18].

Quite recently, we have extended our investigations to the trinuclear complexes $(CO)_5MnRe(CO)_3(bpm)Re(CO)_3Br$ (bpm=2,2'-bipyrimidine) and $Os_3(CO)_{10}$(α-diimine). The former complex with bpm as a bridging ligand possesses two rather strong absorption bands at 490 and 730 nm, respectively. According to the resonance Raman spectra these bands belong to rather pure CT transitions from the different metal fragments. The weakness of the interaction between the MLCT states was also evident from the strong wavelength dependence of the quantum yield for the homolysis reaction. This quantum yield appeared to be highest upon excitation into the 730 nm band which mainly belongs to CT transitions from the Re(d_π) orbitals of the $(CO)_5MnRe(CO)_3$-fragment [19].

The metal-metal bonded complexes discussed so far, all photodecompose after homolysis of the metal-metal bond. In order to find out if such a homolysis reaction could also take place temporarily as in the case of the heterolytic splitting of a metal-nitrogen bond of a chelate such as bipyridine, we have started an investigation of the photochemistry of the clusters $Os_3(CO)_{10}$(α-diimine). Irradiation of $Os_3(CO)_{10}$(bpm) did not give rise to photodecomposition. Flash photolysis showed, however, the formation of an intermediate having the characteristic absorption of $bpm^{\cdot -}$ and a lifetime of 260 ns in THF and less than 20 ns in toluene. It could even be formed as a stable photoproduct by irradiating the complex in a 2-MeTHF glass. For different α-diimine complexes the lifetime of the intermediate increased with decreasing energy of the lowest π^* orbital. Based on these results it is proposed that MLCT excitation of these clusters is followed by homolysis of an Os-Os bond with formation of a biradical that reacts back to give the parent cluster. The stability of the intermediate depends on the coordinating properties of the solvent molecules and the rate of the backreaction is determined by the driving force for the radical coupling reaction [19].

The high, wavelength and temperature independent, quantum yields found for all metal-metal bonded complexes studied so far, do not provide clear evidence for the two-level scheme with strongly interacting $d_\pi\pi^*$(MLCT) and $\sigma_b\pi^*$ states. Of crucial importance in this respect is the selective variation of the relative energies of these states. In order to achieve this variation we have started a photochemical study of the alkyl-complexes $RRe(CO)_3$(α-diimine) and $Ru(X)(R)(CO)_2$(α-diimine) (X=halide).

(ii) Metal-alkyl complexes

Schanze and co-workers have reported that the complexes $RRe(CO)_3$(bpy) (R=Me,Benz) behave similarly as the metal-metal bonded complexes by photodecomposing into radicals with quantum yields close to unity [20]. A different behaviour has recently been observed by us for the complexes $RRe(CO)_3$(R'-DAB) (R=Me,Et,Benz; R'=iPr,tBu) which showed a strong dependence of their photoreactivity on R [13]. The absorption spectrum of a representative complex is presented in Fig. 2. According to the resonance Raman spectra the band at ca. 450 nm belongs to $d_\pi(Re) \rightarrow \pi^*(R'\text{-DAB})$ MLCT transitions and there is no evidence for an allowed $\sigma_b(Re\text{-}R) \rightarrow \pi^*(R'\text{-DAB})$ transition. Upon irradiation into this band both complexes decomposed into radicals $R^\cdot$ and $Re^+(CO)_3(R'\text{-DAB}^{\cdot -})$ which were trapped by t-BuNO and identified by ESR. Just as for the corresponding R_2Zn(R'-DAB) complexes [4], various coupling reactions occurred between the radicals.

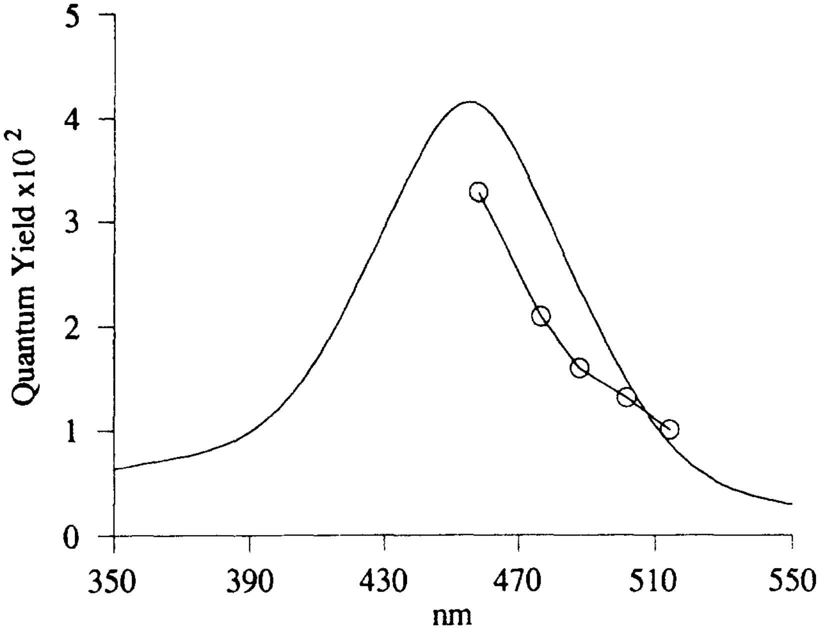


Fig.2 Absorption spectrum and quantum yields for the homolysis reaction of (Me)Re(CO)$_3$(iPr-DAB) in THF.

Contrary to the metal-metal bonded complexes the quantum yield of the homolysis reaction strongly depends on R. For (Me)Re(CO)$_3$(iPr-DAB) it is low (ca. 0.01) and wavelength and temperature dependent (see Fig. 2). The activation energy E_a varies from 10.3 to 7.5 kJmol^{-1} upon changing the wavelength of irradiation from 500 to 460 nm. These results clearly show that this complex, after MLCT excitation, undergoes the homolysis reaction from a reactive state at higher energy, most probably the $^3\sigma_b\pi^*$ state. This proposal is in agreement with the UV-PE spectrum of this complex which shows the σ_b(Re-Me) orbital at a higher Ionization Potential (8.50 eV) than the d_π(Re) orbitals (7.25-7.80 eV).

Going from R=Me to Et or Benz. the quantum yield increases to nearly one and becomes wavelength and temperature independent. This is understandable since the Ionization Potential of σ_b(Re-R) will decrease and so will the energy difference between the $d_\pi\pi^*$ and $\sigma_b\pi^*$ states. Unfortunately, this shift of σ_b(Re-R) could not be verified by the UV-PE spectra since such spectra could not be obtained for the thermally labile ethyl and benzyl complexes.

Just as for the halide (=X) complexes XRe(CO)$_3$(iPr-DAB) the lifetime of the lowest MLCT state of (Me)Re(CO)$_3$(iPr-DAB) is shorter than that of the 10 ns laser pulse. The corresponding ethyl- and benzyl complexes already showed the formation of radicals within the laser pulse when irradiated in THF. When the complex (Benz)Re(CO)$_3$(iPr-DAB) was, however, irradiated in toluene, the time resolved spectra showed the formation of a transient with a lifetime of ca. 280 ns. This transient decomposed into the same radicals as observed in THF. In view of the short lifetimes of the MLCT states and the long lifetimes of the radicals, this transient is assigned to the intermediate $^3\sigma_b\pi^*$ state. Apparently, coordination of THF to the complex in its $^3\sigma_b\pi^*$ state strongly decreases its lifetime. A similar influence of the solvent on the lifetime of a proposed $\sigma_b\pi^*$ state has recently been found by Djurovich and Watts for a series of N,Si-chelated Ir-complexes [21]. The influence of the alkyl group on the photoreactivity of metal-alkyl complexes is not restricted to these Re-complexes. A similar behaviour has been observed by our group for the complexes Ru(X)(R)(CO)$_2$(α-diimine) (X=halide; R=alkyl) [22]. For R=Me and Et the complexes are photostable, for R=iPr they decompose into radicals by homolysis of the Ru-R bond. Again, these radicals could be trapped and identified by ESR. Just as for the Re-complexes the relative energies of the $^3\sigma_b\pi^*$ and $^3d_\pi\pi^*$ states depend on R and the reactive $^3\sigma_b\pi^*$ state can only be occupied for R=iPr.

(iii) Metal-halide complexes

Quite remarkably, there appeared to be a close correspondence between the photochemical behaviour of the metal-metal bonded complexes (CO)$_5$MnMn(CO)$_3$(bpy) and *fac*-XMn(CO)$_3$(bpy) (X=halide) [23]. In both cases irradiation into the visible absorption band produced the dimer Mn$_2$(CO)$_6$(bpy)$_2$. Since this dimer is normally formed by dimerization of 16e-Mn$^+$(CO)$_3$(bpy$^{\cdot-}$) radicals, we have studied in detail the photochemistry of *fac*-XMn(CO)$_3$(bpy) in order to verify the occurrence of a Mn-X homolysis reaction. At room temperature the complexes were first converted into their *mer*-isomers, which then photodecomposed into radicals X· and Mn$^+$(CO)$_3$(bpy$^{\cdot-}$). The latter radicals were trapped and identified by ESR. A more detailed mechanistic study at low temperature showed that the parent *fac*-isomer loses CO by reaction from the lowest ^{3}LF state. The CO-loss product was then converted, thermally and photochemically into the *mer*-isomer, which in turn photodecomposed into radicals Mn$^+$(CO)$_3$(bpy$^{\cdot-}$). These 16-electron radicals were stabilized at low temperature by adduct formation with PR$_3$. At room temperature these adducts initiated the catalytic disproportionation of the parent complex into Mn(CO)$_3$(bpy)(PR$_3$)$^+$ and Br$^-$. A similar catalytic reaction has been observed by us for the complex (CO)$_5$MnMn(CO)$_3$(bpy) [1,18]. All reaction steps are presented in Scheme I.

Of crucial importance are the different primary photoprocesses of the *fac*- and *mer*-isomers. The *fac*-complexes lose CO, the *mer*-isomers undergo an homolysis reaction. The CO-loss reaction most likely occurs from a low-lying ^{3}LF state after surface crossing from the MLCT state(s). Going from the *fac*- to *mer*-isomers the MLCT band shifts to longer wavelength (Fig. 3). This shift to lower energy is most likely responsible for the change of reaction since the reactive ^{3}LF state cannot be occupied anymore. Apparently, the *mer*-isomers then undergo a similar homolysis reaction as the metal-metal and metal-alkyl bonded complexes after surface crossing from the MLCT state(s) to the reactive $^3\sigma_b\pi^*$ state. It is worth mentioning that a similar homolysis reaction has recently been observed by us for the corresponding (Benz)Mn(CO)$_3$(R-DAB) complexes.

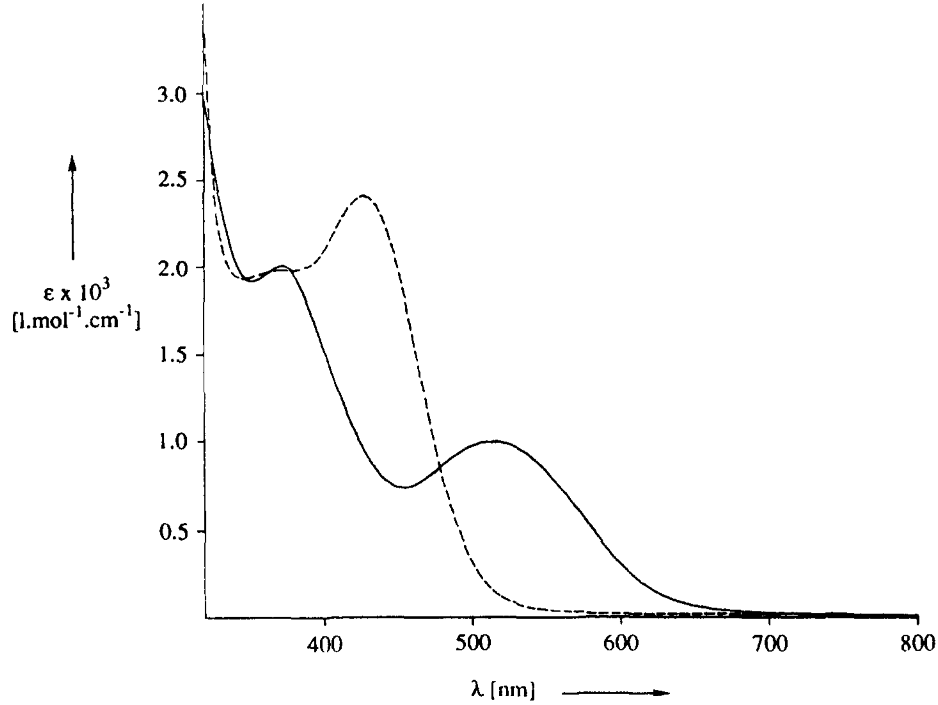
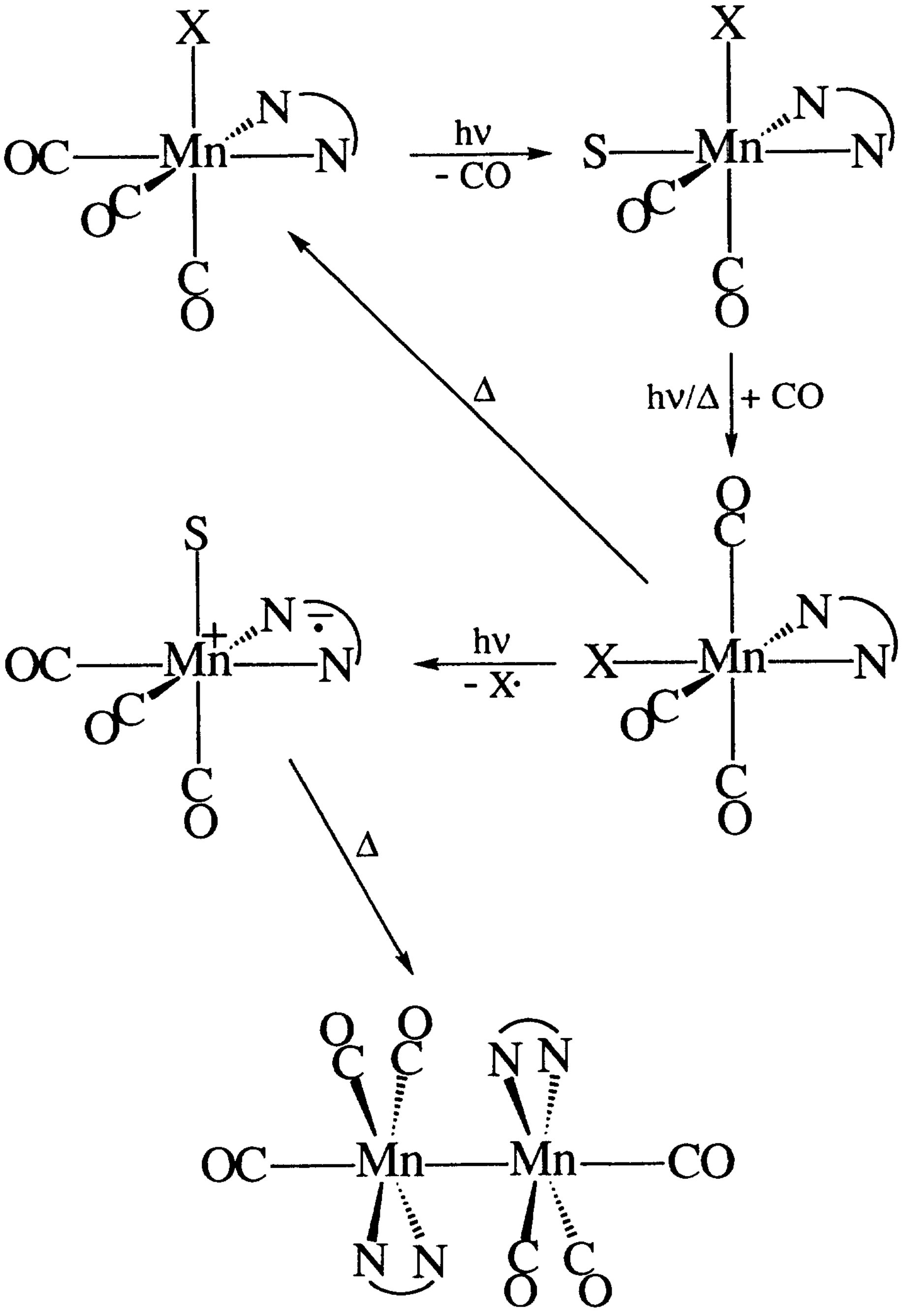


Fig. 3 Electronic absorption spectra of *fac*-(---) and *mer*-BrMn(CO)$_3$(bpy) (———) in THF.



Scheme I

C. CONCLUSIONS

The photochemical data obtained for the alkyl complexes $RRe(CO)_3(R'\text{-}DAB)$ show that the homolysis reaction most likely occurs from a $^3\sigma_b\pi^*$ state after surface crossing from a nonreactive MLCT state. It is shown that homolysis reactions also occur for clusters such as $Os_3(CO)_{10}(\alpha\text{-diimine})$ although without product formation and even in the case of halide complexes such as *mer*-$XMn(CO)_3(bpy)$.

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