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Excited states of metal–metal bonded diimine complexes vary from extremely long lived to very reactive with formation of radicals or zwitterions

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Contents

Abstract

The metal–metal bonded complexes Re(ML_n)$(CO)_3$(α-diimine) [$ML_n = Mn(CO)_5$, $Re(CO)_5$, $SnPh_3$, etc.] have a lowest $^3\sigma\pi^*$ excited state, in which σ represents the Re–M bonding orbital and π^* the lowest empty orbital of the α-diimine. This excited state, which can be occupied via the Re→α-diimine MLCT states, is normally reactive, giving rise to homolysis of the Re–M σ bond. Only the complex Re($SnPh_3$)$(CO)_3$(bpy) was found to be photostable and much longer lived in its $^3\sigma\pi^*$ state than related complexes having a lowest ^{3}MLCT state of comparable energy. This was ascribed to the strength of the Re–Sn bond and to the weak distortion of this complex in its $^3\sigma\pi^*$ state with respect to the ground state.

In the complexes Ru(E)(E′)$(CO)_2$(α-diimine) the axial ligands E and E′ can vary strongly and so do their excited state properties. Of special interest are the compounds in which both E and E′ are SnP_3 ligands, strongly bonded to Ru by a high-lying σ orbital. Because of the

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strength of these bonds and the strong mixing of the σ(Sn–Ru–Sn) orbital with the π*(α-diimine) orbital, the structural effects of the σ→π* transition are small. This is reflected in very small shifts of the CO-stretching vibrations with respect to the ground state and in a very long lifetime of the $^3\sigma\pi^*$ state (τ = 264 μs for $Ru(SnPh_3)_2(CO)_2$(iPr–DAB) in a 2-MeTHF glass at 77 K).

Similarly, irradiation of a cluster $Os_3(CO)_{10}$(α-diimine) in an apolar solvent gives rise to homolysis of an Os–Os bond with formation of a biradical, which was detected with EPR and time-resolved absorption spectroscopy (τ = 5–110 ns). In a coordinating solvent such as CH_3CN, the homolysis reaction is accompanied by the coordination of a solvent molecule, which induces an intramolecular electron transfer. A zwitterion is then formed, which has a lifetime of seconds in CH_3CN. The biradical can also be transformed into such a zwitterion if a Lewis base is added to the apolar solvent. In this article the mechanistic details of these reactions are presented and discussed.

Keywords: Metal–metal bonds; Diimine complexes; Photochemistry; MLCT states; $^3\sigma\pi^*$ states; Radicals; Zwitterions

1. Introduction

Complexes having a lowest and long-lived metal-to-ligand charge-transfer (MLCT) state are often good photosensitizers for light-induced energy and electron transfer processes. Most studied in this respect are $Ru(bpy)_3^{2+}$, its derivatives and the organometallic complexes $Re(L)(CO)_3$(α-diimine)$^{0/+}$. The latter complexes are of special interest since the character of their lowest excited state can be influenced by variation of L. Whereas the lowest excited state has MLCT character for $L = CH_3CN$, this state obtains a ligand-to-ligand charge-transfer (LLCT) character if $L = I^-$ [1] or an organic donor molecule [2,3].

In most cases, complexes having such a low MLCT or LLCT state are not photoreactive. Clear exceptions are complexes such as $Re(ML_n)(CO)_3$(α-diimine) [$ML_n = Mn(CO)_5$, $Re(CO)_5$, $Co(CO)_4$, or $SnPh_3$] [3–14] and $Re(R)(CO)_3$(α-diimine) (R = alkyl) [15–17], in which the metal fragment or alkyl group is bonded to the Re atom by a high-lying σ orbital. The lowest LLCT excited state then obtains a σπ* [18] or sigma-bond-to-ligand charge-transfer (SBLCT) [19] character since an electron is transferred from the metal–metal or metal–alkyl σ-bonding orbital to the lowest π* orbital of the α-diimine.

The properties of these σπ* states are quite different from those of MLCT states. They are not normally optically accessible, but can be reached by surface crossing from the MLCT states. They are often very reactive, giving rise to homolysis of the metal–metal or metal–alkyl σ bond with formation of radicals. In some cases, however, the $^3\sigma\pi^*$ state is not reactive and then much longer lived than the ^{3}MLCT states of closely related complexes. This means that a $^3\sigma\pi^*$ state may vary from reactive to stable and very long lived, depending on the properties of the metal–ligand σ bond. In the next section it will be shown how the lowest $^3\sigma\pi^*$ state varies for a series of metal–metal bonded complexes and which interesting reactions may occur from such a state in the case of metal clusters. The general structures of the complexes and α-dimine ligands used are presented in Fig. 1.

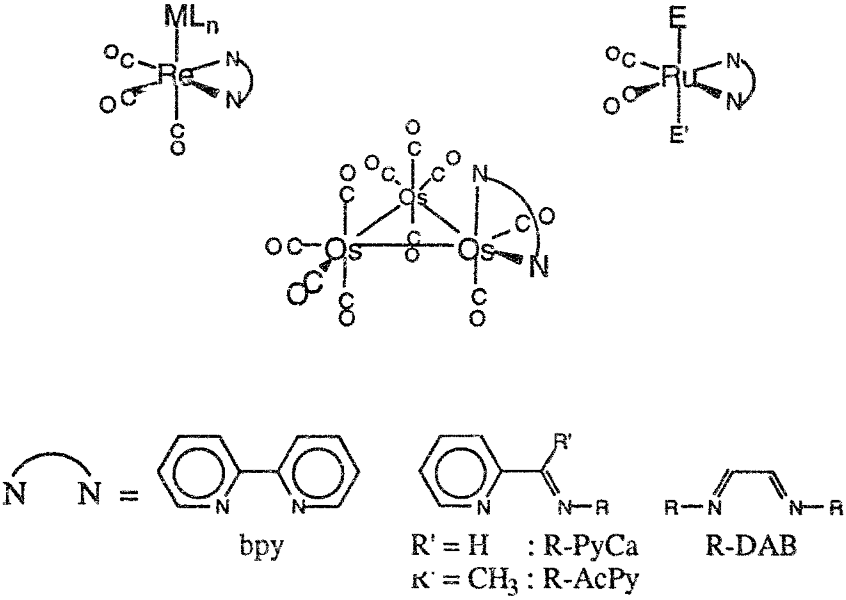


Fig. 1. Structures of the complexes and of the α-diimine ligands 2,2'-bipyridine (bpy), pyridine-2-carbaldehyde-N-R-imine (R-PyCa), 2-acetylpyridine-N-R-imine (R-AcPy), and 1,4-di-R-diazabutadiene (R-DAB).

2. Results and discussion

2.1. Re(ML$_n$)(CO)$_3$(α-diimine) complexes

The excited state properties of these binuclear complexes, in which the metal fragment ML$_n$ represents a Mn(CO)$_5$, Re(CO)$_5$, or SnPh$_3$ group, are completely different from those of related Re(L)(CO)$_3$(α-diimine)$^{0/+}$ complexes having a lowest ^{3}MLCT state. The M(CO)$_5$ (M = Mn, Re)-complexes photodecompose into radicals, an effect which had already been observed by Wrighton and co-workers [4–6] and ascribed by these authors to the presence of a strongly allowed $\sigma \rightarrow \pi^*$ transition and corresponding reactive $^3\sigma\pi^*$ excited state. However, based on its solvatochromism and on the resonance Raman spectra, we have reassigned the intense ($\varepsilon = 4600$–13600 M^{-1} cm^{-1}) absorption band of these complexes to MLCT transitions [3]. The reactive $^3\sigma\pi^*$ state is then occupied via these optically accessible MLCT states.

The $^3\sigma\pi^*$ states of these complexes could be detected both in emission in a glass at 77 K and in the nanosecond (ns) time-resolved absorption (TA) spectra at room temperature [14]. The TA spectra of Re[Mn(CO)$_5$](CO)$_3$(iPr-DAB) in toluene, recorded 25 ns after the 532 nm excitation pulse, show a strong bleach of the ground state absorption and a transient absorbing at approximately 490 nm [see Fig. 2(a)]. This transient decays totally within 100 ns, with retention of the bleach. At the same time a new absorption appears at ca. 390 nm, which is similar to that of the radical

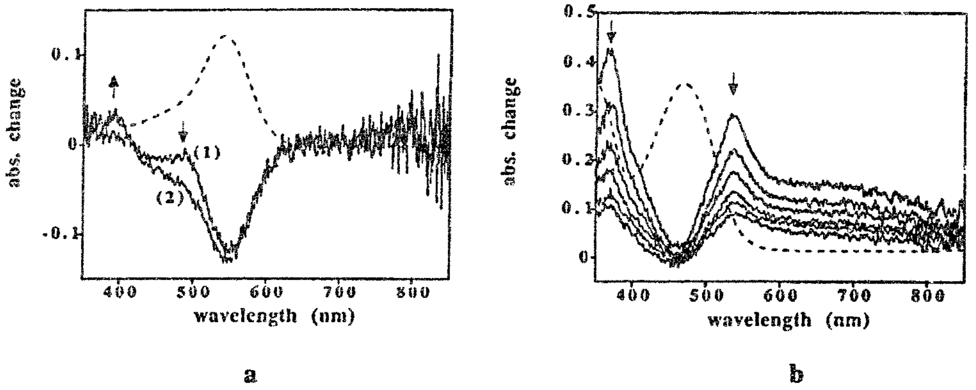


Fig. 2. Nanosecond transient absorption spectra of (a) Re[Mn(CO)$_5$](CO)$_3$(iPr–DAB) in toluene reorded at 25 (curve 1) and 1025 (curve 2) ns after the 532 nm laser pulse (- - - = ground state absorption) and (b) Re(SnPh$_3$)(CO)$_3$(bpy′) in toluene recorded at 20, 270, 520, 770, 1020 and 1270 ns after the 532 nm laserpulse (— = ground state absorption). Adapted from ref. [14].

Re(S)(CO)$_3$(iPr-DAB)· obtained by irradiation of Re(Benzyl)(CO)$_3$(iPr-DAB) [16,17]. The 390 nm band is accordingly assigned to this radical and the 490 nm transient to the $^3\sigma\pi^*$ state from which it is formed. In 2-MeTHF the 490 nm transient was not observed, and the 390 nm band was already present at 20 ns after the laser excitation. Such a dramatic increase of the rate of Mn–Re homolysis upon going to nucleophilic solvents, is a characteristic property of $^3\sigma\pi^*$ states. It has also been observed for Re(Benzyl)(CO)$_3$(iPr-DAB) [17] and for the complexes Re[Mn(CO)$_5$](CO)$_3$(bpy′) (bpy′ = 4,4′-Me$_2$-bpy) and Re[Re(CO)$_5$](CO)$_3$(iPr-DAB) [14].

Quite different behaviour was observed for the related Re(SnPh$_3$)(CO)$_3$(bpy′) complex [14]. Contrary to the M(CO)$_5$ (M = Mn, Re) compounds, this complex is not photoreactive in nonchlorinated solvents, most probably because the bond between Sn and a third-row transition metal is very strong. In agreement with this, the TA spectra show the decay from the $^3\sigma\pi^*$ state (both peaks belong to this state) with a complete regeneration of the ground state [Fig. 2(b)]. Although the metal—metal bond is not broken, the solvent still influences the lifetime of the $^3\sigma\pi^*$ state; it varies from 1100 ns in toluene to 500 ns in THF. These lifetimes are very long compared to those of related complexes having a lowest ^{3}MLCT state. Thus, the ^{3}MLCT state of the related Re(Cl)(CO)$_3$(bpy) complex has a lifetime of only 50 ns at room temperature.

The low-temperature emission data of these metal–metal bonded complexes fully confirm that $^3\sigma\pi^*$ states, that are stable or become so at low temperatures, have much longer lifetimes than ^{3}MLCT states of related complexes [14]. Thus, the complex Re(SnPh$_3$)(CO)$_3$(bpy′) has the following emission properties in a 2-MeTHF glass at 77 K: $\lambda_{em} = 609$ nm, $\Delta E_{(abs-em)} = 6944$ cm^{-1}, $\tau = 106$ µs, $\Phi = 133 \times 10^{-4}$, $k_r = 125$ s^{-1} and $k_{nr} = 0.9 \times 10^4$ s^{-1}. For comparison, Re(Br)(CO)$_3$(bpy′), which has a lowest excited state of a mixed MLCT/LLCT character, has the following emission data: $\lambda_{em} = 525$ nm, $\Delta E_{(abs-em)} = 7907$ cm^{-1}, $\tau = 3.6$ µs, $\Phi = 149 \times 10^{-4}$, $k_r = 4139$ s^{-1}

and $k_{nr} = 27 \times 10^4\ s^{-1}$ [14]. These data show that, although the $^3\sigma\pi^*$ excited state of the SnPh$_3$-complex has a much lower energy than the MLCT/LLCT state of the Br-complex, the k_{nr} value is still by a factor of 30 lower, the lifetime 30 times longer. This difference is not in line with energy gap law (EGL) behaviour and underlines once more the different characters of the excited states of these complexes. This deviation from EGL behaviour is partly due to a large difference in excited state distortion, which is reflected in different values for the apparent Stokes shift $\Delta E_{(abs-em)}$. In accordance with our previous conclusion that the $\sigma \rightarrow \pi^*$ transition can only be a weak contributor to the visible absorption band of these metal–metal bonded complexes [3], the k_r value of the SnPh$_3$-complex is much smaller than that of the Br-compound.

2.2. *Ru(E)(E′)(CO)$_2$(α-diimine) complexes*

The excited state properties can be influenced even more in the case of the complexes Ru(E)(E′)(CO)$_2$(α-dimine), since both axial ligands E and E′ (see Fig. 1) can be varied nearly at will. Thus, complexes have been prepared in which E = halide and E′ = alkyl or metal fragment, and quite different ones in which both E and E′ represent a σ-bonded alkyl ligand or metal fragment [20–31]. Just as the corresponding Re(X)(CO)$_3$(α-diimine) (X = halide) complexes, the halide containing compounds Ru(X)(E′)(CO)$_2$(α-diimine) have a stable lowest-excited state with a varying degree of MLCT/LLCT character depending on X and E′ [20,21,29]. Only if E′ represents a benzyl or isopropyl ligand does the Ru–E′ σ-bonding orbital become so high in energy that the lowest-excited state obtains $^3\sigma\pi^*$ character and the complex becomes photoreactive [22,32]. The MLCT character of the lowest-excited state of Ru(Cl)(Me)(CO)$_2$(iPr-DAB) is evident from its nanosecond time-resolved IR (TRIR) spectra, which show that the CO-stretching vibrations are shifted ca. 50 cm^{-1} to higher frequency with respect to the ground state [25]. For the corresponding Ru(I)(Me)(CO)$_2$(iPr-DAB) complex the mean shift of the CO-stretching vibrations is only ca. 35 cm^{-1}, which points to a lowest-excited state having mixed MLCT/LLCT character since MLCT excitation will, but LLCT excitation will not, affect the metal-to-CO π backbonding.

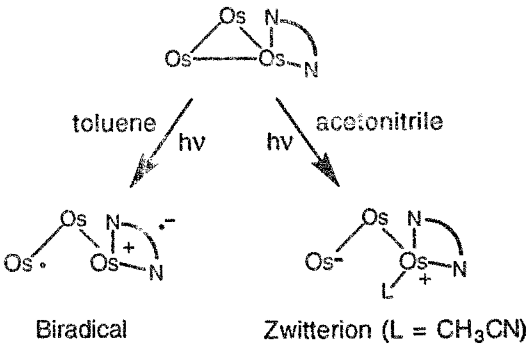
The metal–metal bonded complexes Ru(X)(ML$_n$)(CO)$_2$(α-dimine) (X = halide; ML$_n$ = SnPh$_3$, PbPh$_3$) behave similarly to the other halide complexes [29,31]. They are not photoreactive and their emission data in a glass at 77 K point to a mixed MLCT/LLCT character of their lowest excited state. It is noteworthy that substitution of the methyl ligand in Ru(Cl)(Me)(CO)$_2$(iPr-DAB) by SnPh$_3$ changes the excited state character from MLCT into mixed MLCT/LLCT [29]. This is e.g. evident from the TRIR spectra, which show that the mean shift of the CO-stretching vibrations to higher frequency is only 23 cm^{-1} for Ru(Cl)(SnPh$_3$)(CO)$_2$(iPr-DAB) (Fig. 3, left) [29], whereas it is 50 cm^{-1} for the corresponding methyl-complex [25]. All halide complexes emit in a 2-MeTHF glass at 77 K; their emission lifetimes vary from 300 ns for Ru(Cl)(Me)(CO)$_2$(iPr-DAB) (λ_{em} = 650 nm) [21] to 10 μs for Ru(Cl)(PbPh$_3$)(CO)$_2$(iPr-DAB) (λ_{em} = 634 nm) the synthesis of the complex $Os(SnPh_3)_2(CO)_2(bpy')$, which appeared to be photostable at room temperature. The emission lifetime of this complex in a 2-MeTHF glass at 80 K ($\tau = 230$ μs) is comparable with that of the Ru-complex ($\tau = 264$ μs) (J. van Slageren, Pers. Comm., 1997).

2.3. $Os_3(CO)_{10}$(α-diimine) clusters

The results obtained for the binuclear and linear trinuclear complexes prompted us to study also the photochemistry of substituted clusters of the type $Os_3(CO)_{10}$(α-diimine), the general structure of which is presented in Fig. 1. It had already been established that these clusters also possess MLCT transitions in the visible region [33]. In accordance with the behaviour of the complexes discussed above, MLCT excitation was expected to be followed by occupation of a $^3\sigma\pi^*$ state from which a biradical species might be formed. Just as the radicals formed from the binuclear complexes, the biradical was expected to regenerate the parent cluster, to undergo an electron transfer reaction in coordinating solvents (S) (compare e.g. $\cdot Mn(CO)_5 + Mn(S)(CO)_3(\alpha\text{-dimine})\cdot \rightarrow Mn(CO)_5^- + Mn(S)(CO)_3(\alpha\text{-diimine})^+$ [11,12]) or to afford a ligand-bridged product in case the α-diimine ligand has a reactive imine bond (R-DAB or R-PyCa) [11].

Clusters containing an aromatic α-diimine such as bpy did not transform into a photoproduct upon MLCT excitation [33]. However, in coordinating solvents such as acetonitrile or pyridine, intermediates were formed, which were identified as the zwitterionic species $^-Os(CO)_4$-$Os(CO)_4$-$Os^+(S)(CO)_2$(α-diimine) by IR, UV-Vis, resonance Raman and ^{1}H-NMR spectroscopy [33]. They regenerated the parent cluster. In noncoordinating and weakly coordinating solvents such as toluene or THF no zwitterions were formed. However, according to the time-resolved absorption spectra, short-lived species were still formed, which were identified as biradical species and which also transformed mainly back into the parent cluster [34]. Thus, the $Os_3(CO)_{10}$(α-diimine) clusters show a solvent-dependent photochemistry, which is schematically depicted in Scheme 1 [34].

The mechanisms of these reactions and the properties of the biradicals and zwitterions formed have been studied in detail [34]. Thus, the lifetimes of the



Scheme 1. Solvent dependent photochemistry of the clusters $Os_3(CO)_{10}$ (α-diimine).

zwitterions at room temperature appeared to depend on the coordinating ability of the solvent. They live seconds in nitrile solvents and minutes in pyridine, and they could be stabilized in these solvents at lower temperatures. At room temperature stable zwitterions could only be obtained by adding a salt such as $(nBu)_4Br$ to the solution. Up to now no zwitterions could be isolated and structurally characterized.

However, direct proof for the formation of a charge-separated species was obtained with time-resolved microwave conductivity (TRMC) [35]. For such measurements the sample solution is placed in a microwave field and the change of conductivity of the solution by the formation of a dipolar species is determined [36]. Unfortunately, such measurements are restricted to solutions in apolar media, in which no zwitterions are formed. In order to solve this problem, a cluster was prepared which contained the potentially terdentate ligand Me_2N-$(CH_2)_3$-AcPy coordinated to the metal via the pyridine and imine groups [35]. On irradiation of $Os_3(CO)_{10}(Me_2N$-$(CH_2)_3$-AcPy) a zwitterion was formed even in apolar solvents, which was stabilized by coordination of the Me_2N-$(CH_2)_3$- sidearm to the positively charged metal. The structure of this zwitterion is schematically depicted in Fig. 4; its dipolar character could unambiguously be established with TRMC [35].

Zwitterions might in principle be formed via an associative mechanism, i.e. by the attack of a coordinating solvent molecule at the cluster in its excited state, or via dissociation of the Os–Os bond followed by coordination of a solvent molecule to the biradical. In order to solve this problem, the quantum yield of zwitterion formation was determined for one of these clusters in pyridine as a function of pressure, which was varied from 0.1 to 150 MPa [34]. From these data an activation volume $\Delta V^{\ddagger} = +7.0 \pm 0.5\ \mathrm{cm^3\ mol^{-1}}$ was derived. This means that the mechanism of the zwitterion formation is dissociative but that the effect of bond cleavage is partially offset by coordination of the solvent.

The biradicals formed in apolar solvents could be quenched by nitrosodurene and the resulting adducts were detected with EPR spectroscopy [34]. They were also observed with nanosecond TA spectroscopy and Fig. 5 presents these TA spectra for the reaction of $Os_3(CO)_{10}$(iPr-AcPy) in THF at 298 K [34]. The spectra show a strong bleach at about 540 nm which nearly coincides with the ground state absorption, represented by the dotted curve. There are transient absorptions in the whole spectral region and the lifetime of transient and bleach is the same, viz. 111 ± 5 ns.

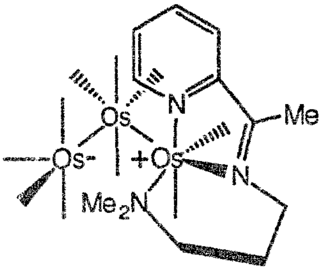


Fig. 4. Schematic structure of the internally stabilized zwitterion $^{-}Os(CO)_4$-$Os(CO)_4$-$Os^{+}(CO)_2(Me_2N$-$(CH_2)_3$-AcPy).

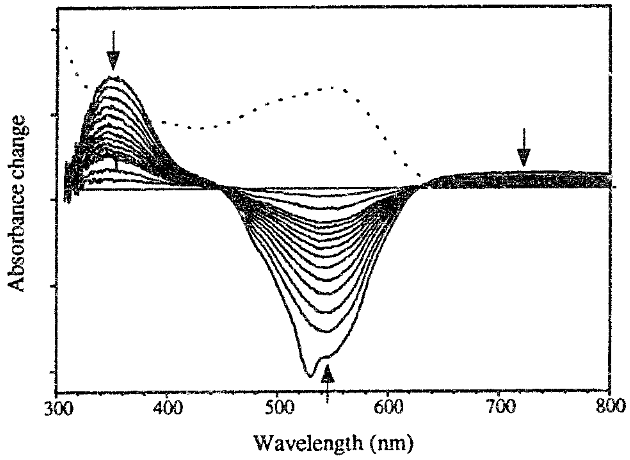


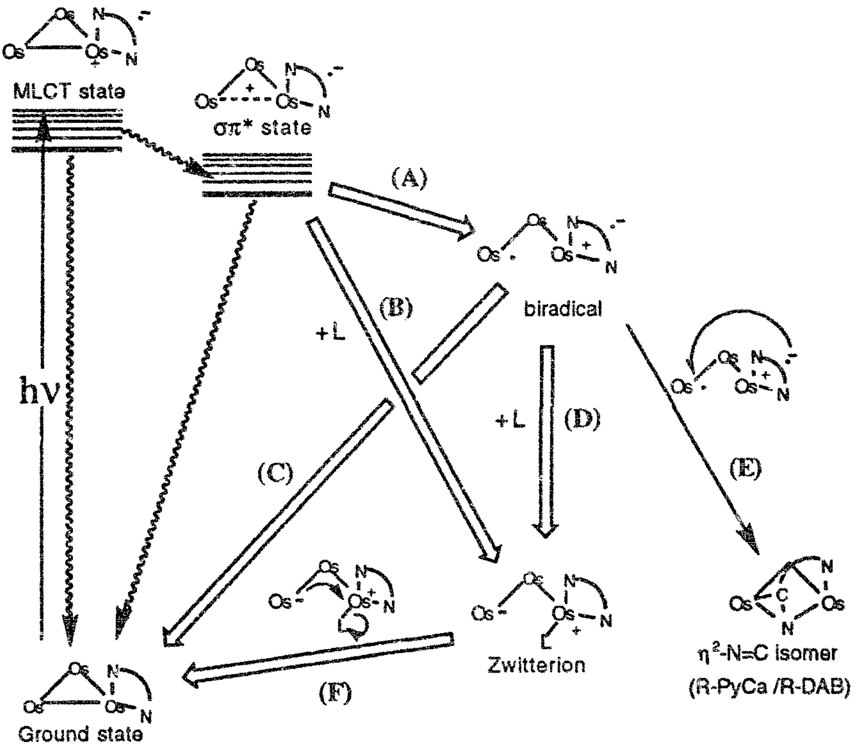
Fig. 5. Nanosecond transient absorption spectra of $Os_3(CO)_{10}$(iPr-AcPy) in THF at 298 K. Time delay between the first 12 spectra is 10 ns, after that it is 30 ns (- - - ground state absorption).

The long-wavelength absorption of the transient is not present in the spectra of the zwitterions and is characteristic of an α-diimine radical anion. The transient absorption has, therefore, been assigned to the biradical species $\cdot Os(CO)_4$-$Os(CO)_4$-$Os^+(CO)_2$(α-diimine·-). As for the zwitterions, the biradicals are stabilized by coordination of a solvent molecule. Thus, the lifetime of the biradical shown in Fig. 5 drops from 111 to 26 to 5 ns upon going from THF to 2-Cl-butane and toluene. Apart from this, the solvent has an appreciable influence on the biradical formation itself, since the transient signals become much weaker in apolar solvents.

Although most biradicals regenerate the parent cluster, a minor part (ca. 5%) transforms into a ligand-bridged isomer if the α-diimine possesses a reactive imine bond (R-PyCa, R-DAB) [37]. The formation of this isomer in which the α-diimine becomes σ, σ bonded to one Os atom and π bonded to another after cleavage of the Os–Os bond, is quite similar to the formation of the ligand-bridged complex $Mn(CO)_4$(σ,σ,π-R-PyCa)$Mn(CO)_3$ after homolysis of the Mn–Mn bond of $Mn[Mn(CO)_5](CO)_3$(R-PyCa) in a viscous medium such as paraffin [11]. The quantum yield of the isomer formation increases with the efficiency of the biradical production, i.e. going from toluene to THF.

It is noteworthy that the biradicals can be transformed into zwitterions. This is already evident from the formation of the internally stabilized zwitterion in the case of $Os_3(CO)_{10}(Me_2N\text{-}(CH_2)_3\text{-}AcPy)$ in apolar solvents, in which only short-lived biradicals can be formed as primary photoproducts. It is also manifested by the reaction of the above-mentioned $Os_3(CO)_{10}$(iPr-PyCa) cluster in THF/0.5 CH_3CN [34]. The TA spectra show the formation of the biradical and its conversion into the long-lived acetonitrile-stabilized zwitterion.

The above results are summarized in Scheme 2 [34]. MLCT excitation is followed by surface crossing to the $^3\sigma\pi^*$ state just as for the binuclear metal–metal bonded complexes. From this state the cluster may decay to the ground state or transform



Scheme 2. Proposed mechanism for the photoreactions of the clusters $Os_3(CO)_{10}$ (α-diimine).

into a biradical, and the latter process (step A) is more efficient in THF than in toluene. A zwitterion may be formed by the uptake of a coordinating solvent molecule such as CH_3CN, either by the cluster in its $^3\sigma\pi^*$ state (step B), or by the biradical (steps A and D). There is no evidence to clarify at which stage during the homolysis reaction from the $^3\sigma\pi^*$ state the solvent molecules induce the charge shift leading to the zwitterion formation, since the volume of activation is positive, but small ($\Delta V^{\ddagger} = +7.0 \pm 0.5\ \mathrm{cm^3\ mol^{-1}}$). Thus, both pathways, B and A+D, are still possible. Steps A and D occur if the photoreaction takes place in a weakly or noncoordinating solvent in the presence of a Lewis base L, which may also be the coordinating sidearm of the α-diimine ligand. A minor part of the biradicals reacts further to give a stable α-diimine-bridged isomer in the case of the R-PyCa and R-DAB clusters (step E). Finally, both the biradicals and the zwitterions regenerate the parent cluster (step C and F, respectively), and in both cases this back reaction is retarded by the coordination of a solvent molecule.

3. Conclusion

The above results show that the $^3\sigma\pi^*$ state of a metal–metal bonded α-diimine complex may vary from very reactive to stable. If it is stable, either because the σ

bond is intrinsically very strong as for the metal–$SnPh_3$ complexes, or on irradiation at low temperature, the complex is much less distorted in this state with respect to the ground state than related complexes in a lowest ^{3}MLCT state. This is, for example, manifested by much smaller k_{nr} values, much longer lifetimes of the excited state, and much smaller shifts of the CO-stretching vibrations.

The radical producing complexes are now under investigation as visible-light photoinitiators of polymerization reactions; those having a very long lived and stable $^3\sigma\pi^*$ state might be good infrared emitters.

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