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Light-induced formation of zwitterions and biradicals from the cluster $[Os_3(CO)_{10}(^iPr\text{-}AcPy)]$ studied with picosecond UV–vis and nanosecond IR spectroscopies

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Contents

Abstract

Ultrafast time-resolved absorption spectra were measured for the cluster $[Os_3(CO)_{10}(^iPr\text{-}AcPy)]$ in several non-coordinating solvents and in MeCN after excitation with visible light. In all solvents, the excited cluster partly converts into biradicals with an excited state lifetime of about 25 ps. In MeCN the cluster undergoes an additional, much faster process ($\tau = 2.9$ ps) that is assigned to zwitterion formation from a solvated excited cluster. Zwitterions are also formed from the biradicals, provided the backreaction of these biradicals to the parent cluster takes longer than about 10 μs due to solvation by a coordinating solvent or added Lewis base. The latter reaction was observed in MeCN and also for some alkene-stabilized biradical products of $[Os_3(CO)_{10}(^iPr\text{-}AcPy)]$.

Keywords: Os-carbonyl clusters; Biradicals; Zwitterions; Picosecond time-resolved UV–vis spectroscopy; Nanosecond time-resolved IR spectroscopy

1. Introduction

Metal–metal bonded complexes such as $[Mn_2(CO)_{10}]$, $[Cp_2Fe_2(CO)_4]$, and $[Cp_2Mo_2(CO)_6]$ undergo CO-loss and homolysis of the metal–metal bond upon irradiation with near-UV light [1–4]. Replacement of two carbonyls in $[Mn_2(CO)_{10}]$ by an α-diimine such as 2,2′-bipyridine produces $[Mn_2(CO)_8(\alpha\text{-diimine})]$ which has additional low-energy electronic transitions to the α-diimine and undergoes the same photoreactions already upon irradiation with visible light [5–7]. Thus, irradiation of $[(CO)_5Mn{-}Mn(CO)_3(\alpha\text{-diimine})]$ in non-coordinating solvents produces the radicals $[^\bullet Mn(CO)_5]$ and $[Mn^+(CO)_3(\alpha\text{-diimine}^{\bullet -})]$, which dimerize [6]. In viscous solvents, where the radicals cannot diffuse from the solvent cage, they react back with each other to regenerate the parent dinuclear complex [6]. In coordinating solvents (Sv) transient radical solvento complexes

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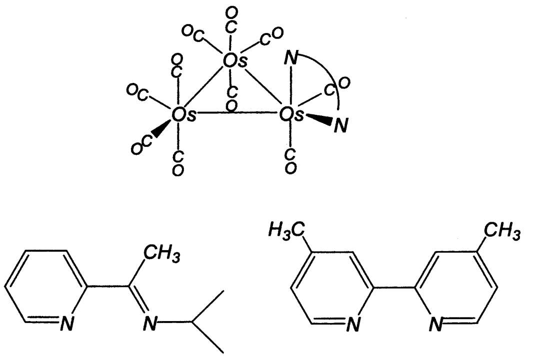
$[Mn^{+}(Sv)(CO)_3(\alpha\text{-diimine}^{\bullet -})]$ are formed which undergo an electron transfer reaction with $[^{\bullet}Mn(CO)_5]$ and $[Mn_2(CO)_{10}]$ to give the ions $[Mn(Sv)(CO)_3(\alpha\text{-diimine})]^{+}$ and $[Mn(CO)_5]^{-}$ [7]. In analogy with these reactions, irradiation of the triangular clusters $[Os_3(CO)_{10}(\alpha\text{-diimine})]$ gives rise to homolysis of an Os–Os(α-diimine) bond, producing biradicals $[^{\bullet}Os(CO)_4–Os(CO)_4–Os^{+}(CO)_2(\alpha\text{-diimine}^{\bullet -})]$ in non-coordinating solvents and zwitterions $[^{-}Os(CO)_4–Os(CO)_4–Os^{+}(Sv)(CO)_2(\alpha\text{-diimine})]$ in coordinating ones [8–11]. The formation of biradicals has been established with nanosecond time-resolved absorption and IR spectroscopies [10] while their nitrosodurene adducts were identified with EPR [9]. The biradical lifetimes vary from nanoseconds to microseconds, mainly depending on the coordinating ability of the solvent or added Lewis base [9,11]. Zwitterions have lifetimes varying from seconds (in MeCN) to minutes (in pyridine), again depending on the coordinating ability of the solvent.

The formation of the biradicals can be understood from the results of DFT calculations of the frontier orbitals and lowest-energy transitions of the $[Os_3(CO)_{10}(\alpha\text{-diimine})]$ clusters [12]. These calculations show that the intense lowest-energy absorption band of these clusters between 500 and 600 nm belongs to several charge transfer transitions from the triosmium core to the α-diimine ligand. The charge-transfer character was confirmed by the resonance Raman spectra obtained by excitation into this absorption band [9]. According to the calculations the main charge transfer transition has $\{\sigma(Os–Os)\rightarrow\pi^{*}(\alpha\text{-diimine})\}$ or sigma-bond-to-ligand charge-transfer (σπ* or SBLCT, [13,14]) character and irradiation into this transition causes a weakening of that Os–Os bond. Although this explained the formation of biradicals, the origin of the zwitterions was still not quite clear. They might be formed directly from the same excited state as the biradicals or at a later stage out of the biradicals. As the reactive excited state was too short lived to be detected by nanosecond time-resolved absorption spectroscopy [9], its transient spectrum and reactions were studied for the representative cluster $[Os_3(CO)_{10}(^{i}Pr\text{-AcPy})]$ (**1**) in the picosecond time domain in apolar, polar and coordinating solvents [11]. For comparison, the same measurements were performed for $[Os_3(CO)_{10}(dmb)]$ (dmb = 4,4′-dimethyl-bipyridine) (**2**) in 2-chlorobutane (2-ClBu) [11]. In order to study the possible conversion of biradicals into zwitterions, the photochemistry of **1** was also investigated in the microsecond time domain in acetonitrile and in 2-ClBu in the presence of the strongly coordinating ligands cyclohexene, 1-octene and styrene [10,11]. The general structure of the $[Os_3(CO)_{10}(\alpha\text{-diimine})]$ clusters and of the α-diimine ligands used are depicted in Fig. 1.



^{i}Pr-AcPy (**1**) dmb (**2**)

Fig. 1. Schematic molecular structures of the clusters $[Os_3(CO)_{10}(\alpha\text{-diimine})]$ and the α-diimine ligands.

2. Results

2.1. Ultrafast time-resolved visible spectroscopy

Picosecond transient absorption (ps TA) spectra of cluster **1** were measured in 2-chlorobutane (2-ClBu), CH_2Cl_2, THF and MeCN, and those of cluster **2** in 2-ClBu [11]. The spectra were obtained by excitation into the visible absorption band of the cluster with a 130 fs/505 nm laser pulse; the spectral changes were measured in the wavelength region 510–700 nm. A detailed description of the equipment used is given in ref. [11]. The TA spectra of **1** in 2-ClBu measured 5–70 ps after the laser pulse are depicted in Fig. 2. Kinetic profiles were probed at 540 nm (bleach) and 630 nm (absorption) and the lifetimes derived from them are collected in Table 1.

The TA spectrum of **1** in 2-ClBu, obtained at $t_d = 5$ ps (Fig. 2), shows a bleach at about 570 nm, close to the maximum of the ground state absorption, and a transient absorption with a maximum at 630 nm. Both the bleach and absorption decay with a lifetime of 25 ± 2 ps, which process mainly involves decay from the $\sigma(Os–Os)\rightarrow\pi^{*}(\alpha\text{-diimine})$ ($^{3}SBLCT/^{3}\sigma\pi^{*}$) excited state to the

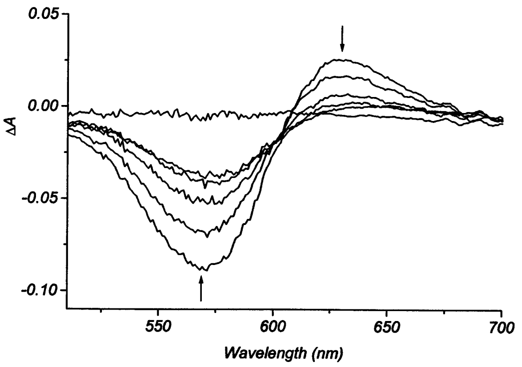


Fig. 2. Transient difference absorption spectra of $[Os_3(CO)_{10}(^{i}Pr\text{-AcPy})]$ (**1**) in 2-ClBu, measured at time delays of –5(baseline), 5, 15, 30, 50, and 70 ps, respectively, after 505 nm, 130 fs FWHM excitation.

Table 1
Lifetimes (τ) of the transients of $[\mathrm{Os_3(CO)_{10}}(\alpha\text{-diimine})]$ in different solvents, derived from their kinetic profiles probed at 630 nm (unless noted otherwise)

Compound	Solvent	τ (ps)
$[\mathrm{Os_3(CO)_{10}}({}^{i}\mathrm{Pr\text{-}AcPy})]$ (**1**)	2-ClBu	26.6/25.3 [a]
	CH_2Cl_2	25.9/24.8 [a]
	THF	20.6
	MeCN	2.9/21.4 (1:3) [b]
$[\mathrm{Os_3(CO)_{10}(dmb)}]$ (**2**)	2-ClBu	0.6/5.0 (5:2) [b]

[a] $\lambda_{\mathrm{probe}} = 540$ nm.
[b] Biexponential behavior with the ratio in brackets.

Table 2
Lifetimes (τ) of the solvent- and alkene-stabilized biradical photoproducts (**1a**) of the cluster $[\mathrm{Os_3(CO)_{10}}({}^{i}\mathrm{Pr\text{-}AcPy})]$ (**1**)

Solvent–alkene	τ (ns)
Toluene	5
2-ClBu	25(2)
2-MeTHF	40(2)
THF	111(5) [a]
Acetone	860(50) [a]
2-ClBu–cyclohexene (1.0 M)	4300(100)
2-ClBu–1-octene (1.0 M)	12 900(500) [a]
2-ClBu–styrene (1.0 M)	14 200(200)

[a] The lifetimes obtained from the TRIR experiments are τ(1-octene–**1a**) = 17000(200) ns, τ(acetone–**1a**) = 930(70) ns, τ(THF–**1a**) = 130(15) ns.

ground state. However, the bleach and the transient absorption do not disappear completely. After 70 ps the intensity of the bleach has merely decreased to ca. 30% of its initial value and part of the transient absorption has transformed into the much broader and less distinct absorption of a second species in the same wavelength region. No further changes were observed in the TA spectra up to 750 ps and the remaining transient absorption is very similar to that observed in the nanosecond TA spectra of **1** [9]. As the broad absorption above 600 nm is rather specific for complexes in metal-to-diimine excited states and for radical ions of (partly) aromatic diimines [15–20], it was assigned to the biradical species $[{}^{\bullet}\mathrm{Os(CO)_4{-}Os(CO)_4{-}Os^{+}(CO)_2}(\alpha\text{-diimine}^{-\bullet})]$. This assignment has been confirmed by the EPR spectra of the trapped biradicals [9] and by nanosecond time-resolved IR spectroscopy [10]. Thus, in non- and weakly coordinating solvents cluster **1** partly decays from its excited state to the ground state and partly decomposes into a biradical species. It is noteworthy that in non- and weakly coordinating solvents the kinetic profiles are all monoexponential and give rise to the same excited-state lifetime (Table 1). The rather long lifetime of about 25 ps indicates that the reaction does not proceed from a dissociative state but that the ^{3}SBLCT/${}^{3}\sigma\pi^{*}$ excited state has a small barrier for the reaction, which is also evident from the temperature dependence of the quantum yield of this photoreaction [9,11]. The excited state of the corresponding dmb-cluster **2** has a much shorter lifetime of 5 ps. The kinetic profile of **2** shows a second, very fast, process that most probably represents partial decomposition of the cluster into biradicals before the relaxed excited state is reached.

In MeCN the decay of the transient absorption of **1** is biexponential, with lifetimes of 2.9 and 21.4 ps contributing to the decay in a ratio 1:3. The lifetime of 21.4 ps closely resembles that of cluster **1** in noncoordinating solvents (vide supra and Table 1) and is accordingly assigned to the decay to the ground state and to biradical formation. The short lifetime is not observed in the non-coordinating solvents and is assigned to the formation of zwitterions from the solvated excited state of the cluster (see Section 3).

2.2. Microsecond time-resolved UV–vis and IR spectroscopies

According to the ns TA studies the biradicals formed as the only primary photoproducts of **1** in non- and weakly coordinating solvents, regenerate the parent cluster with lifetimes that strongly depend on the coordinating ability of the solvent, the lifetime being shortest in 2-ClBu and longest in acetone (Table 2) [9,10]. Table 2 also shows that the lifetime is still longer when 1.0 M cyclohexene, 1-octene or styrene is added to the solution of **1** in 2-ClBu [10]. This comparison points to a strong Os–olefin bond in the biradical. From these alkene-biradicals, the cyclohexene-biradical is shorter lived and regenerates the parent cluster, whereas the 1-octene- and styrene-biradicals live longer and transform into a different species. In order to assign the latter products, the photoreaction of **1** in 2-ClBu in the presence of octene (1.0 M) was followed with ns and μs time-resolved IR (TRIR) spectroscopy in the CO-stretching region [10]. The spectrum recorded 1 μs after the laser pulse was different from that of the parent cluster but very similar to the TRIR spectra of the biradicals formed upon irradiation of **1** in acetone, THF and 2-ClBu and recorded 40–70 ns after the laser pulse [10]. The only difference is that the ν(CO) frequencies of the 1-octene-stabilized biradical are somewhat higher than those of the others because of the π-backbonding to the alkene. The TRIR spectrum of this solution recorded 75 μs after the laser pulse is completely different from that of the biradical but very similar to the spectrum of the long-lived zwitterions formed by the photoreaction of **1** in acetone at 213 K or in 2-ClBu in the presence of 1-octene at 223 K (Fig. 3) [10]. This result shows that in the case of 1-octene (and styrene) the biradicals do not regenerate the parent cluster anymore but transform into zwitterions. This process

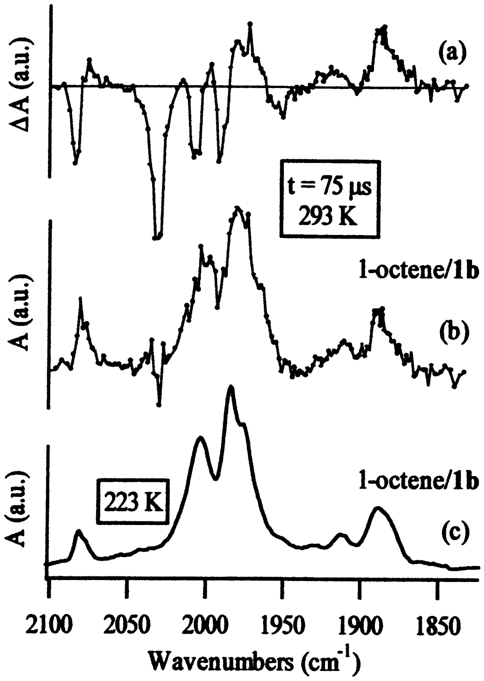


Fig. 3. Nanosecond TRIR difference spectrum of the zwitterion formed by irradiation of $[Os_3(CO)_{10}(^iPr\text{-}AcPy)]$ (**1**) in 2-ClBu in the presence of 1-octene (1.0 M), recorded 75 μs after the laser pulse at 293 K (a), the corresponding TRIR product spectrum after subtraction of the FTIR spectrum of the parent cluster (b), and the FTIR spectrum of the corresponding stable zwitterion (1-octene–**1b**) formed in 2-ClBu at 223 K.

is slow and can only compete with the backreaction to the parent cluster when the latter reaction takes longer than 10 μs. This is nicely demonstrated by the different behavior of the cyclohexene- and 1-octene- (and styrene-) biradical adducts.

In view of these experiments with the alkenes we extended our photochemical studies of cluster **1** in MeCN to the nanosecond and microsecond time domain. The ns kinetic traces of **1** in MeCN did not show any change with respect to those in the ps time domain. This means that the biradicals formed in this solvent do not regenerate the parent cluster in this time domain. However, on the microsecond time scale the bleach partly disappears with a lifetime of 20 μs (Fig. 4); in agreement with the behavior of the alkene-coordinated biradicals we attribute this effect to a conversion of the MeCN-stabilized biradicals into the corresponding zwitterions. The decrease of the bleach is caused by the fact that in contrast to the biradicals, the zwitterions absorb in the same wavelength region (around 560 nm) as the parent cluster.

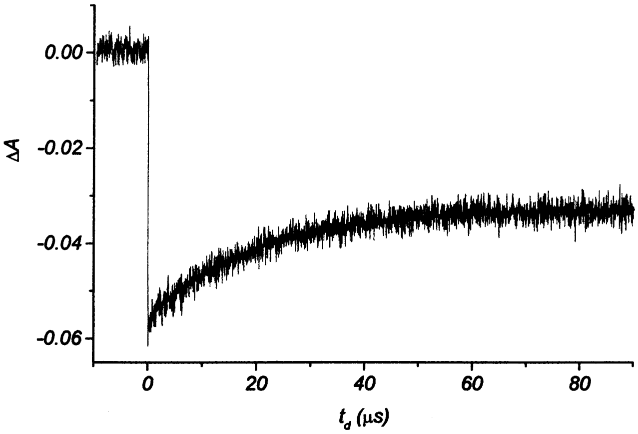
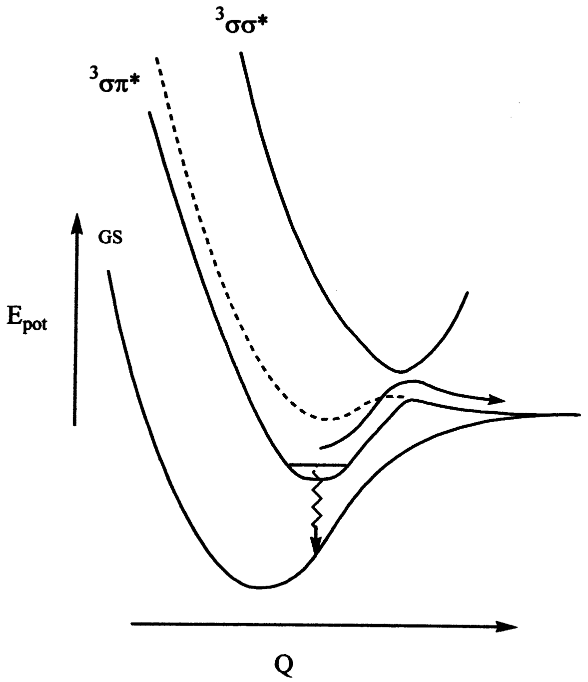


Fig. 4. Transient kinetics at 560 nm measured in the microsecond time domain for $[Os_3(CO)_{10}(^iPr\text{-}AcPy)]$ (**1**) in MeCN following irradation at 532 nm (Nd:YAG, 7 ns FWHM).

This process not only occurs in MeCN or in the presence of alkenes, it is also observed for $[Os_3(CO)_{10}\{Me_2N(CH_2)_3\text{-}AcPy\}]$ in which the pendant $Me_2N(CH_2)_3-$ sidearm may act as a Lewis base just as MeCN. The biradicals of this cluster have a lifetime of 11.3 μs in CH_2Cl_2 and were also found to convert into zwitterions.

3. Discussion

The ps TA spectra show that cluster **1** undergoes decay to the ground state and conversion into biradicals with a lifetime of about 20 ps [12]. This rather long lifetime indicates that the reaction does not proceed from a dissociative state but that the ^{3}SBLCT/$^3\sigma\pi^*$ excited state has a small barrier for the reaction, probably to a repulsive $^3\sigma\sigma^*$ state of the Os_3 core. The presence of this barrier is also evident from the temperature dependence of the quantum yield of this photoreaction [9,11] and is further confirmed by the shorter lifetime of the excited state of the corresponding dmb cluster **2**. As the dmb ligand has its lowest π^* orbital at higher energy than ^{i}Pr–AcPy, the ^{3}SBLCT/$^3\sigma\pi^*$ state of **2** will be higher in energy than that of **1**, whereas their $^3\sigma\sigma^*$ states are most likely the same since the two clusters contain the same Os_3 core. This causes a lowering of the barrier and a concomitant decrease of the lifetime from 25 to 5 ps going from **1** to **2**. This process of biradical formation is schematically depicted in Scheme 1. This scheme clearly shows that the increase of energy of the ^{3}SBLCT/$^3\sigma\pi^*$ state going from **1** to **2** results in a lowering of the barrier between that state and the $^3\sigma\sigma^*$ state, causing the observed shortening of the excited state lifetime. In principle, the height of the barrier may be derived from the calculated excited-state potential energy curves of the cluster along the Os–Os bond. However, such calculations have only been performed up to now for more simple complexes. For instance, Daniel and co-workers recently calculated the dissociation barrier for the Ru–Sn bond in the ^{3}SBLCT state of the linear trinuclear complex $[Ru(SnH_3)_2(CO)_2(Me\text{-}DAB)]$[21], a model complex of $[Ru(SnPh_3)_2(CO)_2(\alpha\text{-diimine})]$, for which a similar in-

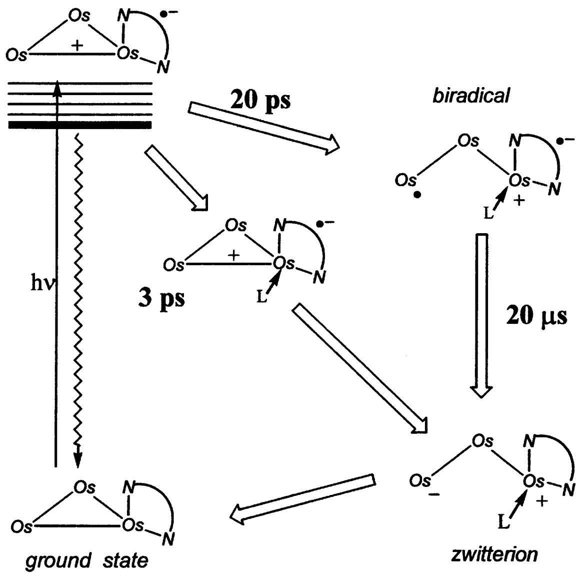


Scheme 1. Qualitative potential–energy curves and reaction dynamics of $[Os_3(CO)_{10}(^i\text{Pr-AcPy})]$ (**1**) (—) and $[Os_3(CO)_{10}(dmb)]$ (**2**) (-----) in the excited states.

fluence of the α-diimine on the excited state lifetime was found as for the Os clusters under investigation [14].

A different behavior was observed for cluster **1** in MeCN. The ps TA spectra measured in this solvent not only showed a similar decomposition into biradicals as in the other solvents, there was also a much faster process. A similar solvent effect on the excited-state lifetime has been observed for other metal–metal bonded α-diimine complexes such as $[(CO)_5Mn\text{-}Re(CO)_3(^i\text{Pr-DAB})]$ (^{i}Pr-DAB = 1,4-diisopropyl-1,4-diaza-1,3-butadiene) [15]. In toluene the ns TA spectra of this complex show the absorption of the ^{3}SBLCT/$^3\sigma\pi^*$ excited state, which decays totally within 100 ns with formation of radicals. However, in 2-MeTHF the absorption of this state is not observed anymore and the radicals are already present directly after the 7 ns laser pulse.

In order to understand the nature of this solvent-induced process, we recall the ns time-resolved microwave conductivity (TRMC) measurements on a related cluster in which the ^{i}Pr-group of the ^{i}Pr-AcPy ligand in **1** was replaced by the pendant sidearm $Me_2N(CH_2)_3$- [22]. Laser excitation of a cyclohexane solution of $[Os_3(CO)_{10}\{Me_2N(CH_2)_3\text{-AcPy}\}]$ caused the formation of a conductivity transient already within the 7 ns laser pulse. This implies that the solution contains a photoproduct having a dipole moment larger than that of the cluster in its ground state. Because of this dipolar character, the photoproduct has been assigned to the zwitterion $[^-Os(CO)_4\text{–}Os(CO)_4\text{–}Os^+(CO)_2\{Me_2N(CH_2)_3\text{-AcPy}\}]$, in which the $Me_2N(CH_2)_3$-sidearm coordinates to the electron-deficient metal center of the $\{Os^+(CO)_2\{Me_2N(CH_2)_3\text{-AcPy}\}$ moiety. A similar photoreaction will occur for **1** in MeCN. As the TA spectra of **1** in MeCN did not show any further change up to 750 ps, formation of the zwitterions is proposed to occur in the early picosecond time domain and to be responsible for the very short lifetime of 2.9 ps derived from the kinetic profile of the transient absorption of **1** in this solvent. In view of this short lifetime we propose that for $[Os_3(CO)_{10}\{Me_2N(CH_2)_3\text{-AcPy}\}]$ in cyclohexane as well as for **1** in MeCN the zwitterions are formed out of the excited state by intramolecular charge separation induced by coordination of the $Me_2N(CH_2)_3$– sidearm and MeCN, respectively, to the $Os^+(CO)_2(\alpha\text{-diimine}^{\bullet -})$ site. Thus, cluster **1** undergoes two primary photoprocesses in MeCN, viz. homolysis of an Os–Os bond with formation of biradicals just as in noncoordinating solvents ($\tau = 21.4$ ps) and heterolytic splitting of an Os–Os bond resulting in the formation of zwitterions ($\tau = 2.9$ ps). These two processes take place from different types of excited clusters. The first type, giving rise to the formation of biradicals, is the cluster in its non-solvated excited state, since the reaction is the same for all solvents. The second type represents the solvated excited cluster (exciplex) in which the strong σ-donor MeCN is coordinated to the $\{Os^+(CO)_2(^i\text{Pr-AcPy}^{\bullet -})\}$ moiety of the excited cluster. This solvation will induce the heterolytic splitting of the Os–Os(α-diimine) bond and give rise to zwitterion formation. These two processes are presented schematically in Scheme 2. To our knowledge no other metal clusters are known to undergo heterolytic splitting of a



Scheme 2. Schematic representation of the photoprocesses of $[Os_3(CO)_{10}(^i\text{Pr-AcPy})]$ (**1**) in MeCN (= L) together with their lifetimes.

metal–metal bond in the excited state. Quite recently, however, an interesting solvent-induced photodisproportionation has been observed for Hg_2^{2+} [23].

The biradicals regenerate the parent cluster, provided their lifetime, which increases with the coordinating ability of the solvent or added reactant, is not longer than about 10 μs. Thus, the cyclohexene-coordinated biradical of **1**, which has a lifetime of about 4 μs, still regenerates the parent cluster, whereas the corresponding styrene- or 1-octene- coordinated biradicals, having lifetimes of 10–15 μs, transform into zwitterions as manifested by TRIR spectroscopy. Because of the strong coordination of MeCN, an analogous reaction occurs for the corresponding MeCN-coordinated biradicals within a lifetime of 20 μs.

A similar increase of lifetime can be achieved by performing the photoreaction of **1** in a weakly coordinating solvent such as acetone or THF at lower temperatures. At room temperature this photoreaction gives rise to the formation of biradicals which regenerate the parent cluster, whereas zwitterions are formed upon irradiation at temperatures below 243 K (acetone) and 223 K (THF), respectively [10].

The two ways of zwitterion formation, viz. directly from the solvated excited state and via the biradicals, are schematically depicted in Scheme 2. Ultimately, all excited states and biradicals that are solvated by a strongly coordinating solvent, convert into zwitterions. The quantum yield of the photoreaction is only restricted by the fraction of excited clusters that undergo a non-productive decay to the ground state. In view of the decay of the bleach (Fig. 2) and the fact that the biradicals hardly absorb in the 550–600 nm region, we conclude that about one third of **1** produces zwitterions, which agrees with the quantum yield of about 0.3 for the zwitterion formation of this cluster in pyridine [9].

4. Conclusions

Irradiation into the visible absorption band of the clusters $[Os_3(CO)_{10}(\alpha\text{-diimine})]$ gives rise to the formation of biradicals, in agreement with the $\{\sigma(Os{-}Os) \rightarrow \pi^*(\alpha\text{-diimine})\}$ character of their lowest-energy transition. The nature and efficiency of this reaction is not influenced by the polarity of the solvent but changes when a coordinating solvent such as MeCN is used. Such solvents may form exciplexes and transform the cluster into a zwitterion. In addition, MeCN and other Lewis bases slow down the back reaction of the biradicals to the parent clusters to such an extent that these biradicals convert instead into zwitterions, which is a second, much slower, way of producing these species. The most interesting result of these studies is that for the first time a heterolytic splitting of a metal–metal bond directly from the excited state has been established.

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