Photo- and redox activation of homo-and heteronuclear transition metal clusters: experiment and theory
Vergeer, F.W.

Citation for published version (APA):
Chapter 4

Part C

Redox-Controlled Charge-Transfer Photochemistry of $[\text{Os}_3(\text{CO})_{10}(\text{AcPy-MV}^{2+})]$ (AcPy-MV$^{2+}$ = [2-pyridylacetimine-N-(2-(1'-methyl-4,4'-bipyridin-1,1'-diium-1-yl)-ethyl)](PF$_6$)$_2$)
4C.1 Abstract

(Sub)picosecond transient absorption and time-resolved infrared spectra of the novel purpose-designed cluster $[\text{Os}_3(\text{CO})_{10}\text{AcPy-MV}^2\text{+}]$ reveals that photoinduced electron transfer to the electron accepting $4,4'$-bipyridinium moiety competes with the fast relaxation of the initially populated $\sigma\pi^*$ excited state of the cluster to the ground state and biradicals. The TA spectra of $\text{I}^{2+}$ in acetone, obtained by irradiation into its lowest-energy absorption band, show characteristic intense absorptions of the one-electron-reduced $\text{MV}^+$ unit at 400 and 610 nm. The latter absorption bands are assigned to a charge-separated (CS) state in which an electron has been transferred from the cluster core to the lowest $\pi^*$ orbital of the $\text{MV}^{2+}$ moiety. This assignment is confirmed by time-resolved IR spectra on the picosecond time scale which, in agreement with the photooxidation of the cluster core, show a shift of the highest-frequency $\nu(\text{CO})$ band to larger wavenumbers by $ca. 40 \text{ cm}^{-1}$ with respect to the corresponding ground-state band. The CS state is populated via fast $(4.4 \times 10^{11} \text{ s}^{-1})$ and efficient (> 92%) oxidative quenching of the optically populated $\sigma\pi^*$ excited state and decays bi-exponentially, upon nearly complete regeneration of the parent cluster, with lifetimes of 43 and 180 picoseconds (3:2 ratio).

The photochemical behaviour of $\text{I}^{2+}$ can be controlled by an externally applied electronic bias. Irradiation of $\text{I}^{2+}$ in acetonitrile results in the formation of a stable photoproduct, that, in line with the independently proven photooxidation of the cluster core, is proposed to result from a similar cluster core-to-$\text{MV}^{2+}$ electron transfer process as observed in acetone. Electrochemical one-electron reduction of the $\text{MV}^{2+}$ moiety prior to irradiation reduces its electron-accepting character to such an extent, that photoinduced electron transfer to the latter unit is no longer feasible. Instead, irradiation of cluster $\text{I}^{2+}$ results in reversible formation of zwitterions, the ultimate photoproduct observed upon irradiation of the clusters $[\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})]$ in strongly coordinating solvent. Based on the observed photochemical behaviour of the redox couple $\text{I}^{2+}$ and $\text{I}^{+}$, the $[\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})]\text{-MV}^{2+}$ (donor-acceptor) dyad can be designated as a molecular redox switch.

4C.2 Introduction

The control of electron transfer reactions through specific (non-)covalent interactions is a general phenomenon in many biological processes, such as respiration and photosynthesis. Aimed at understanding the fundamental principles underlying the often remarkable quantum efficiencies of these reactions, considerable research efforts have been devoted to the design of supramolecular systems capable of mimicking, at the molecular level, the functions normally performed by a natural system. As examples may serve light-harvesting antenna
systems, \cite{1-5} artificial reaction centres, \cite{6-10} molecular switches \cite{11} etc. As the function displayed by such artificial molecular devices generally results from the interplay of the intrinsic performances of their specific components, the assembly of the latter in the topologically and energetically correct way is, just as in their biological counterparts, of major importance.

A particular type of molecular devices concerns those using absorbed light as the energy source. Their function commonly relies on energy- or electron-transfer processes taking place between the different components of the supramolecular assembly. Critical for their effective functioning is the competition between productive and non-productive electron transfer processes, where the non-productive electron transfer usually concerns the fast back electron transfer prior to the response of the system to the photoinduced charge separation. For example, photoexcitation of the Ru(II) chromophore in a TiO$_2$-Rh(III)-Ru(II) heterotriad results in stepwise charge separation, the first electron transfer step TiO$_2$-Rh(III)-*Ru(II) $\rightarrow$ TiO$_2$-Rh(II)-Ru(III) having an efficiency close to unity.\cite{12} Further charge separation via electron injection into the semiconductor, is, however, only 40% efficient because of a competing charge recombination process. Another example concerns the reversible movement of a macrocycle between two binding stations in a photochemically driven molecular shuttle. Dependent on the rate of charge recombination, transitory motion of the ring may either be very efficient \cite{13} or not observed at all.\cite{14}

Another important development in the field of molecular electronics focuses on the creation of ultrafast 'molecular scale' computers, incorporating devices capable of high-density data transport close to the speed of light. As photoinduced energy- and electron transfer processes can occur on the sub-picosecond time scale, the design of molecules performing switching (YES/NO) and other logical operations via optical inputs has received considerable attention. Apart from energy- or electron transfer reactions themselves, the switching of physical properties may also result from coupled selective bond-breaking or -making processes. The reversible rearrangement processes in transition metal clusters, selectively triggered by external stimuli such as light absorption or redox reaction (see Chapter 1), together with the numerous possibilities to functionalize the cluster core, make the cluster systems promising candidates for connector elements in switchable junction devices. When purpose-selected clusters are used as the active switchable components, the significant structural and electronic reorganization of the cluster core upon an external stimulus may reversibly interrupt the communication between chemically attached donor and acceptor termini (Scheme 1). As an alternative approach, changing the electronic properties of the cluster junction by attachment of a (redox) switchable unit may influence the communication between the donor and acceptor sites in a similar way (Scheme 2). Aimed at the realization of the latter system, we focus in the first instance on the response of the cluster core to the changed state of the switchable unit without the donor and acceptor moieties attached.
Scheme 1. Reversible interruption of the communication between donor (D) and acceptor (A) termini in a supramolecular system, employing a cluster core as the active switchable component.

Scheme 2. Reversible interruption of the communication between donor (D) and acceptor (A) termini by attachment of a (redox) switchable trap (T) to the cluster junction.

Combining the recent challenges in the field of molecular electronics with our continued interest in the photochemical reactivity of α-diimine-substituted transition metal clusters, we herein report on the synthesis, photochemical and electrochemical reactivity of the novel cluster \([\text{Os}_3(\text{CO})_{10}(\text{AcPy-MV}^{2+})]\) (AcPy-MV\(^{2+}\) = \([2\text{-pyridylacetimine-N-(2-(1'-methyl-4,4'-bipyridin-1,1'-diium-1-yl)-ethyl})\text{(PF}_6\text{)}_2\text{]}\text{(I}^2\text{+)}\) (Figure 1). The strongly electron accepting 4,4'-bipyridin-1,1'-diium (viologen) unit is covalently linked to the imine nitrogen of the α-diimine ligand.
Redox-Controlled Charge-Transfer Photochemistry of [Os₆(CO)₁₀(AcPy-MV²⁺)]

Figure 1. Schematic structures of the cluster [Os₆(CO)₁₀(AcPy-MV²⁺)] (1²⁺) and the α-diimine ligand used in this study.

Picosecond transient absorption and time-resolved infrared spectra were recorded in order to investigate whether photoinduced electron transfer to the remote viologen moiety and concomitant formation of a charge-separated state can compete with the fast decay of the initially populated σπ* excited state to the ground state and biradicals (25 ps, see part A). Similar electron transfer reactions have been observed for several viologen-linked [Ru(bpy)₃]²⁺ complexes, although the lifetime of the ³MLCT excited state of the latter complexes is extended into the nanosecond time domain. In a second step, we focused on the redox control of the charge separation in [Os₆(CO)₁₀(AcPy-MV²⁺)], with the aim to restore the characteristic photoreactivity of the normal [Os₆(CO)₁₀(α-diimine)] clusters (see Part A). A combined photo- and electrochemical study was performed in order to monitor this process. In this study, the structurally related cluster [Os₆(CO)₁₀(Pr-AcPy)], where the alkyl-linked viologen unit is replaced by an isopropyl substituent, served as a proper reference.

4C.3 Experimental

Materials and preparation. [Os₆(CO)₁₂] (Strem Chemicals), 4,4ʹ-bipyridyl (Fluka), 2-pyridinecarboxaldehyde (Acros), 2-bromoethylamine hydrobromide, piperidine (Aldrich) and ferrocene (BDH) were used as received. Trimethylamine-N-oxide dihydrate, Me₃NO-2H₂O (Janssen), was dehydrated prior to use by vacuum sublimation. Solvents of analytical grade (Acros: ethanol (EtOH), methanol (MeOH), hexane, diethylether (Et₂O), CH₂Cl₂, acetonitrile (MeCN)) and spectroscopic grade (Acros: acetone) were dried over sodium (EtOH, MeOH, Et₂O, hexane), CaH₂ (CH₂Cl₂, MeCN) and B₂O₃ (acetone) and freshly distilled under a nitrogen atmosphere prior to use. Neutral aluminium oxide 90 (70-230 mesh, Merck) for column chromatography was activated by heating in vacuo at 450 K overnight and stored under N₂. The supporting electrolyte Bu₄NPF₆ (Aldrich) was recrystallized twice from ethanol and dried in vacuo at 350 K overnight.
Synthetic procedures. All syntheses were performed under an inert atmosphere of dry nitrogen, using standard Schlenk techniques. The precursors [1-methyl-4,4'-bipyridin-1-ium] and [1-(2-aminoethyl)-1'-methyl-4,4'-bipyridin-1,1'-diium][PF$_6$]$_2$ and the cluster [Os$_3$(CO)$_{10}$(MeCN)$_2$]$_2$ were prepared according to published procedures and were characterized by $^1$H NMR and FT-IR spectroscopies. The synthetic route towards cluster 1 is depicted in Scheme 3.

Scheme 3. Synthesis of cluster 1$^{2+}$.

Synthesis of [2-pyridylacetimine-N-(2-(1'-methyl-4,4'-bipyridin-1,1'-diium-1-yl)-ethyl)](PF$_6$)$_2$ (AcPy-MV$^{2+}$). A mixture of [1-(2-aminoethyl)-1'-methyl-4,4'-bipyridin-1,1'-diium][PF$_6$]$_2$ (385 mg, 0.76 mmol), 2-pyridinecarboxaldehyde (200 μl, 1.8 mmol) and piperidine (a few drops) in EtOH (5 ml) was refluxed for 1.5 h in the presence of 3 Å molecular sieves. After this period the solvent was removed in vacuo and the residue was washed with 5 x 10 ml Et$_2$O. The ligand was isolated as an off-white solid in 66% yield. $^1$H NMR (d$_6$-acetone) (for numbering scheme see Figure 1): δ 9.59 (d, $^3$J = 6.6 Hz, 2H, H$_7$), 9.36 (d, $^3$J = 6.6 Hz, 2H, H$_{10}$), 8.87 (d, $^3$J = 6.6 Hz, 2H, H$_7$), 8.81 (d, $^3$J = 6.6 Hz, 2H, H$_7$), 8.66 (d, $^3$J = 4.5 Hz, 1H, H$_4$), 8.21 (d, $^3$J = 8 Hz, 1H, H$_4$), 7.94 (dd, $^3$J = 8 Hz, $^3$J = 7.5 Hz 1H, H$_3$), 7.56 (dd, $^3$J = 4.5 Hz, $^3$J = 7.5 Hz 1H, H$_3$), 5.41 (t, $^3$J = 5.1 Hz , 2H, H$_5$), 4.74 (s, 3H, N-CH$_3$), 4.36 (t, $^3$J = 5.1 Hz, 2H, H$_5$), 2.49 (s, 3H, C-CH$_3$).

Synthesis of [Os$_3$(CO)$_{10}$(AcPy-MV$^{2+}$)](PF$_6$)$_2$ (1$^{2+}$). A solution of [Os$_3$(CO)$_{10}$(MeCN)$_2$] (220 mg, 0.24 mmol) and AcPy-MV$^{2+}$ (230 mg, 0.37 mmol) in acetone (25 ml) was stirred in the dark for 16 h. After this period the solvent was removed in vacuo. The crude product was purified by column chromatography over aluminium oxide using CH$_2$Cl$_2$/MeCN gradient elution. Cluster 1$^{2+}$ was obtained as a deep red solid in 20% yield. IR ν(CO) (MeCN): 2089 (m), 2040 (s), 2002 (vs), 1986 (s), 1964 (sh), 1893 (w) cm$^{-1}$. $^1$H NMR (d$_6$-acetone) (for numbering scheme see Figure 1): δ 9.57 (d, $^3$J = 5.4 Hz, 1H, H$_7$), 9.50 (d, $^3$J = 7.2 Hz, 2H, H$_{10}$), 9.39 (d, $^3$J = 6.9 Hz, 2H, H$_7$), 8.89 (d, $^3$J = 7.2 Hz, 2H, H$_7$), 8.78 (d, $^3$J = 6.9 Hz, 2H, H$_7$), 8.54 (d, $^3$J = 7.9 Hz, 1H, H$_4$), 8.19 (dd, $^3$J = 7.5 Hz, $^3$J = 8.1 Hz, 1H, H$_3$), 7.58 (dd, $^3$J = 7.5 Hz, $^3$J = 5.7 Hz, 1H, H$_3$), 5.65 (ddd, $^3$J = 13 Hz, $^3$J = 4.2 Hz, $^3$J = 3.9 Hz, 1H, H6/6'), 5.50 (ddd, $^3$J = 14 Hz, $^3$J = 4.2 Hz, $^3$J = 3.9 Hz, 1H, H5/5'), 5.41 (ddd, $^3$J = 13 Hz, $^3$J = 9.6 Hz, 1H, H4/4')}
Redox-Controlled Charge-Transfer Photochemistry of [Os$_3$(CO)$_{10}$(AcPy-MV$^{2+}$)]

Hz, $^3J = 3.9$ Hz, 1H, H6/6$'$), 5.02 (ddd, $^2J = 14$ Hz, $^3J = 9.6$ Hz, 2H, H5/5$'$), 4.75 (s, 3H, N-CH$_3$), 3.08 (s, 3H, C-CH$_3$). UV-vis (acetone): 373 (sh), 554 nm. FAB$^+$ MS (m/z): 1482 [M+Na]$^+$, 1315.55 [M-PF$_6$]$^-$ (calc. 1315.0), 1170 [M-2PF$_6$]$^-$.

**Spectroscopic measurements.** FT-IR spectra were recorded on Bio-Rad FTS-7 and Bio-Rad FTS-60A spectrometers (16 scans at 2 cm$^{-1}$ resolution), the latter being equipped with a dual-source Digital Model 896 interferometer and a nitrogen-cooled MCT detector. The sample compartment of the Bio-Rad FTS-60A spectrometer was modified to allow in situ laser irradiation into a thermostated cell. UV-vis absorption spectra were recorded on a Hewlett-Packard 8453 diode-array spectrophotometer, $^1$H and $^13$C NMR spectra on a Bruker AMX 300 spectrometer and Fast Atom Bombardment (FAB) mass spectra on a JEOL JMS SX/SX102A four-sector mass spectrometer.

**Photochemistry.** The 514.5 nm line of a Spectra Physics Model 2016 argon-ion laser was used for the continuous-wave irradiation experiments. All photochemical samples were prepared under a nitrogen atmosphere, using standard inert-gas techniques, and typically $10^{-3}$-$10^{-4}$ mol dm$^{-3}$ cluster concentrations.

Nanosecond transient absorption (ns TA) spectra were obtained by irradiating the samples with 2 ns pulses of the 550 nm line (typically 5 mJ/pulse) of a tunable (420-710 nm) Coherent Infinity XPO laser. Picosecond transient absorption (ps TA) spectra were recorded using the setup installed at the University of Amsterdam. Part of the 800 nm output of a Ti-sapphire regenerative amplifier (1 kHz, 130 fs, 1 mJ) was focussed into a H$_2$O flow-through cell (10 mm; Hellma) to generate white light. The residual part of the 800 nm fundamental was used to provide 505 nm (fourth harmonic of the 2020 OPA idler beam) excitation pulses with a general output of 5 $\mu$J pulse$^{-1}$. The picosecond time-resolved infrared (ps TRIR) experiments were carried out at the Central Laser Facility of the Rutherford Appleton Laboratory. In this case, part of the 800 nm output of a Ti-sapphire regenerative amplifier (1 kHz, 150 fs, 2 mJ) was used to provide 500 nm pulses for excitation of the sample. Further experimental details of the time-resolved absorption and IR set-ups are described in Chapter 2.

**Electrochemistry.** Cyclic voltammograms (CV) of approximately $10^{-3}$ M cluster in $10^{-1}$ M Bu$_4$NPF$_6$ electrolyte solution were recorded using the set-up described in Chapter 2. IR and UV-vis spectroelectrochemical measurements were performed in previously described optically transparent thin-layer electrochemical (OTTLE) cells.

**4C.4 Results and Discussion**

**Synthesis**

The novel cluster [Os$_3$(CO)$_{10}$(AcPy-MV$^{2+}$)]$^{2+}$ was synthesized via a three-step reaction sequence and characterized by IR and NMR spectroscopies and mass spectrometry. The IR spectrum of I$^{2+}$ in MeCN closely resembles that of the related cluster [Os$_3$(CO)$_{10}$(Pr-AcPy)], the v(CO) bands being slightly shifted to higher frequencies. This trend is attributed
to a slightly decreased π-backbonding towards the carbonyl ligands due to the reduced basicity of the α-diamoine ligand. The 1H NMR spectrum of 12+ in d6-acetone shows the characteristic resonances of the methylviologen unit and the ethylene linkage. In accordance with the electron-accepting character of the viologen moiety, the proton signals of the α-diamoine moiety are slightly shifted to lower field compared to those of [Os3(CO)10(Pr-AcPy)]. The spectroscopic data therefore provide convincing evidence for the same chelate coordination of the AcPy-MV2+ ligand to the triosmium core as for 1Pr-AcPy.25 The coordination of the AcPy-MV2+ ligand to the cluster core was confirmed by the FAB' MS spectrum of 12+.

Electronic absorption spectra

The UV-vis absorption spectra of 12+ are characterized by a dominant lowest-energy band with its maximum shifted from 558 nm in acetone to 576 nm in CH2Cl2. Similar to its analogue [Os3(CO)10(Pr-AcPy)],25 the lowest-energy absorption band of 12+ encompasses several charge-transfer transitions from the triosmium core to the α-diamoine ligand, denoted as σ(Os-Os) → π*(α-diamoine). Irradiation into the latter band will therefore result in the population of the lowest σπ* excited state in which one of the Os-Os(α-diamoine) bonds is weakened. The small red shift of the lowest-energy band compared to that of [Os3(CO)10(Pr-AcPy)] (viz. 536 nm in acetone) is attributed to a lower energy of the lowest π*(α-diamoine) orbital due to the electron withdrawing methylviologen side-arm.

Ultrafast transient absorption measurements

Picosecond transient absorption (ps TA) spectra of cluster 12+ in acetone were obtained by excitation at 505 nm and detection of the spectral changes in the wavelength region 400-650 nm. Kinetic profiles were probed at 560 nm in 200 fs intervals up to 10 ps, and at 600 nm in 5 ps intervals up to 750 ps. The TA spectra measured at 1-91 ps after the 130 fs laser pulse are depicted in Figure 2. The kinetic profile of 12+, probed at 600 nm, is shown in Figure 3.

The TA spectrum at t = 1 ps (Figure 2) shows an intense absorption at ca. 400 nm and a broad, long-wavelength absorption with a maximum at about 615 nm. The observed absorption bands are characteristic for the one-electron-reduced methylviologen (MV+) unit26 and are therefore assigned, in accordance with the results of the picosecond TRIR experiments (vide infra), to a charge-separated (CS) state in which an electron has been transferred from the cluster core to the lowest π* orbital of the viologen moiety. Within the first few picoseconds the TA spectra show increased absorbance in the region 500-610 nm, the maximum of the long-wavelength absorption being shifted from 615 nm to 606 nm. These spectral changes are attributed to the continued formation of the viologen-localized CS state, most likely via oxidative quenching of the initially populated 3σπ* state. Similar oxidative quenching of an initially populated 3MLCT state is known to form such CS states in several
[Ru(R-bpy)₂(bpy-MV)]⁺⁺ (bpy = 2,2'-bipyridine) complexes, where a viologen unit is covalently linked at the 4-position of one of the bipyridine ligands. On longer time scales (up to 300 ps), the transient absorptions due to the temporarily reduced MV⁺⁺ unit decay bi-exponentially with nearly complete regeneration of the parent cluster. In agreement with the reversibility of the system, the latter process is ascribed to the thermal back electron transfer from the viologen moiety to the cluster core.

![Figure 2](image.png)

**Figure 2.** Transient difference absorption spectra of cluster 1⁺⁺ in acetone measured at time delays of -9 (baseline), 1 (—), 6, 36 and 91 ps, respectively, after 505 nm, 130 fs FWHM excitation.

The kinetics of the viologen-localized CS excited state was studied in more detail by measuring absorbance-time profiles. Assuming that population of the CS excited state indeed takes place via fast decay of the optically populated σπ* excited state (*vide infra*), the forward electron transfer rate constant (k₉) can be derived from a single-exponential fit to the latter process. Unfortunately, an extensive overlap between the transient absorption bands belonging to the σπ* excited state and the characteristic absorptions of the methylviologen radical cation prevents the lifetime of the σπ* excited state to be accurately determined from the experimental data. However, as the absorbance-time profile of 1⁺⁺, probed at 560 nm, shows no further increase of the absorption band due to the viologen radical cation (MV⁺⁺) after 10 ps, the viologen-localized CS state is most likely formed for more than 90% within this period. Based on this assumption the rate constant k₉ is estimated to have a lower limit of 4 x 10¹¹ s⁻¹. As the photoinduced forward electron transfer reaction is much faster than the decay of the CS state, the back electron transfer rate constant (k₉) may be obtained from the decay kinetics of the 606 nm band (Figure 3). The latter band decays bi-exponentially (a feature commonly encountered and probably related to conformational freedom at the ethylene linkage) with lifetimes of 43 ps (60%) and 180 ps (40%) that correspond to back electron transfer rate constants k₉ of 2.3 x 10¹⁰ and 5.6 x 10⁹ s⁻¹, respectively.
Figure 3. Kinetic profile of the difference absorbance of cluster 1^{2+} in acetone at 600 nm, after 505 nm, 130 fs FWHM excitation.

**Picosecond time-resolved IR spectroscopy**

The transient UV-vis spectra provide only limited information about the forward electron-transfer kinetics and the pathway along which the CS state is populated. For this reason, the primary events after the photoexcitation of cluster 1^{2+} were studied with picosecond time-resolved infrared (ps TRIR) spectroscopy. The ps TRIR spectra of cluster 1^{2+} in acetone were recorded after excitation at 500 nm at several pump-probe delays between 0 and 500 ps. Representative difference IR spectra in the region 2200-2020 cm\(^{-1}\) are shown in Figure 4.

Due to the low symmetry of cluster 1^{2+}, its ground-state IR spectrum displays a considerable number of \(\nu(\text{CO})\) bands. An extensive overlap between the bleached \(\nu(\text{CO})\) bands of the parent complex and the transient absorption bands of the excited state precludes the determination of the excited-state CO-stretching frequencies to a large extent. Only the well-separated highest-frequency \(\nu(\text{CO})\) band at 2088 cm\(^{-1}\) can therefore be used to monitor the changes in the electron density on the cluster core upon population of the excited state. After irradiation into the lowest-energy absorption band of 1^{2+} in acetone, the spectra at early time delays (< 3 ps) display instantaneous bleaching of the parent \(\nu(\text{CO})\) bands together with broad transient absorptions due to the excited state of 1^{2+}. The highest-frequency ground-state band at 2088 cm\(^{-1}\) shifts to larger wavenumbers in the excited state. In fact, at \(t_d = 1\) ps (Figure 4b) two broad transient absorption bands are observed on the high-frequency side of the 2088 cm\(^{-1}\) bleach, having their absorption maxima at 2099 and 2121 cm\(^{-1}\), respectively. Within the first few picoseconds (< 10 ps), the transient absorption bands in the terminal \(\nu(\text{CO})\) region sharpen up and slightly shift (ca. 6 cm\(^{-1}\)) to higher frequency. These spectral changes are attributed to early relaxation processes (cooling or solvation) associated with the decay of low-frequency M-C stretching and M-C-O bending vibrational modes populated upon excitation.\(^{29,32}\)
Redox-Controlled Charge-Transfer Photochemistry of [Os₃(CO)₁₀(AcPy-Mt²⁺)]

Figure 4. (a) Difference ps TRIR spectrum of [Os₃(CO)₁₀(Pr-AcPy)] in acetone at \( t_d = 3 \) ps after 500 nm excitation (ca. 150 fs FWHM, 5 µJ pulse⁻¹); (b-e) difference ps TRIR spectra of cluster \( \text{I}^{2+} \) in acetone at (b) 1, (c) 2, (d) 5 and (e) 15 ps after 500 nm excitation (ca. 150 fs FWHM, 5 µJ pulse⁻¹).

On the same time scale, the 2121 cm⁻¹ band further develops at the expense of the 2099 cm⁻¹ band, being gradually shifted to 2127 cm⁻¹ and reaching its maximum intensity at around 10 ps. On a longer time scale (up to 500 ps), the 2127 cm⁻¹ band also decays and the parent cluster becomes almost completely regenerated. The position of the 2099 cm⁻¹ band, shifted to larger wavenumbers by ca. 11 cm⁻¹ with respect to the highest-frequency ground-state band, is in good agreement with that of the highest-frequency transient \( \nu(CO) \) band in the TRIR spectrum of [Os₃(CO)₁₀(Pr-AcPy)] at \( t_d = 3 \) ps (2093 cm⁻¹, Figure 4a). In accordance with the results for the latter cluster (see Chapter 4, Part A), the 2099 cm⁻¹ band is therefore ascribed to \( \text{I}^{2+} \) in its \( 3\sigma^* \) excited state, the shift to larger wavenumbers resulting from decreased \( \pi \)-backdonation to the carbonyl ligands due to depopulation of a \( \sigma(\text{Os-Os}) \) bonding orbital. Upon decay of the 2099 cm⁻¹ band, the \( \nu(CO) \) band at 2121 cm⁻¹ further develops and shifts to larger wavenumbers by ca. 40 cm⁻¹ with respect to the highest-frequency ground-state band. The shift of the latter \( \nu(CO) \) band is indicative of a second, more significant decrease in the \( \pi \)-backdonation that is consistent with formal one-electron oxidation of the cluster core. For, similar shifts of the highest-frequency \( \nu(CO) \) band to larger wavenumbers are observed upon (electro)chemical oxidation of the related clusters [Os₃(CO)₁₀(α-diimine)] (vide infra). In line with the proposed photooxidation of the cluster core, the 2121 cm⁻¹ band is ascribed to a charge-separated (CS) excited state in which an electron has been transferred from the cluster core to the remote viologen unit. As the latter band grows in at the expense of the 2099 cm⁻¹ band, the TRIR spectra clearly prove that population of the CS excited state indeed takes place via fast decay of the optically populated \( \sigma\pi^* \) state. The absence of the 2121 cm⁻¹ band
in the TRIR spectrum at $t_d = 0$ ps, recorded with the excitation and analyzing pulses arriving simultaneously, supports this conclusion and excludes direct optical population of the CS excited state. The relatively small shift (11 cm$^{-1}$) of the $\nu$(CO) bands in the $\sigma\pi^*$ excited state compared to that observed in the CS state (40 cm$^{-1}$) is mainly ascribed to the electron-donating capacity of the temporarily reduced $\alpha$-diimine ligand, partly compensating the decreased $\pi$-backdonation in the $\sigma\pi^*$ state. Upon population of the CS state, the electron residing on the $\alpha$-diimine moiety is transferred to the remote viologen acceptor site, leaving the cluster core formally one-electron-oxidized. Importantly, the TRIR data also prove that from the relaxed $\sigma\pi^*$ excited state hardly any non-radiative decay to the ground state takes place. This is inferred from the observation that the ground-state bleach at 2038 cm$^{-1}$ only shows a minor decrease in signal intensity within the first 5 ps following excitation. This behaviour is in contrast with the results for $[\text{Os}_3(\text{CO})_{10}(\text{Pr-AcPy})]$, where ca. 70% of the molecules in the $\sigma\pi^*$ state decay non-radiatively to the ground state (Chapter 4, Part A), and demonstrates the efficiency of the subsequent electron transfer to the viologen moiety.

In order to get more insight into the kinetics of the CS state, the well-separated transient $\nu$(CO) band at 2121 cm$^{-1}$ was selected for Gaussian curve fitting. Spectral fitting, while fixing the width of the latter band, allowed the peak areas to be determined. A plot of the peak area of the 2121 cm$^{-1}$ band for each time delay against time allows determination of both the $\sigma\pi^*$ excited-state lifetime ($\tau = 2.1 \pm 0.2$ ps) that corresponds to the development of the 2121 cm$^{-1}$ band, and the lifetime of the CS state (75 $\pm$ 10 ps). The $\sigma\pi^*$ excited-state lifetime (2.1 $\pm$ 0.2 ps) has been used to determine the forward electron transfer rate constant $k_f$ according to Eq. (1), with $\tau_{\text{ref}}$ (= 25 ps) being the $^3\sigma\pi^*$ excited-state lifetime of the structurally related cluster $[\text{Os}_3(\text{CO})_{10}(\text{Pr-AcPy})]$ under the same experimental conditions.

$$ k_f = 1/\tau - 1/\tau_{\text{ref}} \quad (1) $$

The resulting value $k_f = 4.4 \times 10^{11}$ s$^{-1}$ is in good agreement with the lower limit derived from the TA experiments. The lifetime of the CS excited state also compares reasonably well with the result obtained from the ps TA measurements. One has to realize, however, that cooling processes complicate to some extent the determination of the excited-state lifetime in the TRIR experiments.

**Nanosecond transient absorption spectroscopy**

Excitation into the lowest-energy transition of $[\text{Os}_3(\text{CO})_{10}(\text{Pr-AcPy})]$ in non- or weakly coordinating solvents (toluene, THF, acetone) results in homolytic splitting of an Os-Os($\alpha$-diimine) bond and concomitant formation of open-structure biradicals (See Chapter 4, Parts A and B). In order to prove whether the formation of similar biradical photoproducts from the relaxed $\sigma\pi^*$ excited state is also feasible for cluster $1^{2+}$, nanosecond transient absorption (ns
TA) spectra of the latter cluster were recorded in acetone. The ns TA spectra were obtained by irradiation of cluster $1^{2+}$ by the 550 nm line of a tunable Coherent Infinity XPO laser and spectral changes were monitored in the wavelength region 350-800 nm. The TA spectra recorded directly after the laser pulse revealed a weak bleaching between 430 and 615 nm due to disappearance of $1^{2+}$, and very weak transient absorptions below 430 nm and in the long wavelength region. On longer time scales (up to 1.5 μs) the transient species almost completely converts back to cluster $1^{2+}$. As the ns TA spectra of $1^{2+}$ closely resemble those of $[\text{Os}_3(\text{CO})_{10}(\text{AcPy})]^{3+}$ in acetone, the observed transient absorptions are accordingly assigned to the open-structure biradical $[\text{Os(CO)}_4\text{Os(CO)}_4^{2+}\text{Os(S)(CO)}_2(\text{AcPy}=\text{(CH}_2)_2\text{-MV}^{2+})]\text{(PF}_6)_2$ (S = acetone). Based on a comparison between the ΔA values observed for $1^{2+}$ and those obtained after irradiation of an isosbestic solution of $[\text{Os}_3(\text{CO})_{10}(\text{Pr-AcPy})]$, the amount of biradicals formed from the σπ* excited state of $1^{2+}$ is reduced by approximately 85%. Assuming similar molar absorptivities for both biradicals, the quantum yield for the biradical formation out of $1^{2+}$ is calculated, using the value obtained for $[\text{Os}_3(\text{CO})_{10}(\text{Pr-AcPy})]$ (0.4, see Chapter 4, Part A), to be approximately 6%. The latter value is in good agreement with the observed shortening of the σπ* excited state lifetime from 25 ps for $[\text{Os}_3(\text{CO})_{10}(\text{Pr-AcPy})]$ to 2.1 ps for $1^{2+}$. Based on this result, approximately 92% of the molecules rapidly decay to the lower-lying CS excited state.

**Scheme 4.** Qualitative excited-state potential energy curves and reaction dynamics of cluster $1^{2+}$ in acetone.

The decay processes for optically excited cluster $1^{2+}$ are schematically depicted in terms of the qualitative potential energy curves in Scheme 4. In agreement with the results of the TRIR experiments, irradiation into the lowest-energy absorption band of $1^{2+}$ results in the initial population of a σπ* excited state, in which one electron has been transferred from the
cluster core to the lowest \( \pi^*(\alpha\text{-diimine}) \) orbital. From this excited state a minor part (6\%) of the cluster molecules produces biradicals whereas the major part (92\%) undergoes fast decay to the charge-separated (CS) state in which the excited \( \pi^*(\alpha\text{-diimine}) \) electron has been transferred to the remote viologen site. Interestingly, the latter electron transfer process (4.4 x 10^{11} \text{s}^{-1}) is considerably faster than the photoinduced electron transfer in related derivatives of \([\text{Ru(bpy)}_3]^{2+}\), where a viologen acceptor unit is attached via comparable amide- or saturated carbon linkages at the 4-position of one of the 2,2'-bipyridine ligands.\(^{15-18}\) For example, a rate constant of merely 3.9 x 10^{10} \text{s}^{-1} has been determined in acetonitrile for a \((\text{dmb}^-\text{-MV}^{2+}) \rightarrow \text{MV}^{2+}\) electron transfer in the \(^3\text{MLCT}\) excited state of \([\text{Ru(dmb)}_2\{4-(2-(1'\text{-methyl-4,4'-bipyridin-1,1'-diium-1-yl)-ethyl}-4'\text{-methyl-2,2'-bipyridine}\}] \) \((\text{dmb} = 4,4'\text{-dimethyl-2,2'-bipyridine})\) possessing an identical ethylene linkage.\(^{17}\) In fact, the value of \(k_f\) for \(1^{2+}\) more closely resembles those obtained for \([\text{Ru(bpy)}_3]^{2+}\) derivatives in which the linkage to the viologen consists of merely a single carbon atom (1.3-2.5 x 10^{11} \text{s}^{-1}).\(^{17}\) Caution should, however, be taken when comparing systems with different energetics for the electron transfer, a different nature of the donor-acceptor linkage and a different solvent system.

The Gibbs energy change (\(\Delta G^{\circ}_{\text{CS}}\)) related to the forward electron transfer reaction, is given by Eq. (2), with D and A representing the cluster core and the viologen unit, respectively.

\[
\Delta G^{\circ}_{\text{CS}} = e(E_{\text{ox}}(D) - E_{\text{red}}(A)) - E_{\text{00}}
\]  

Besides the standard redox potentials \((\text{vide infra})\), the calculation of \(\Delta G^{\circ}_{\text{CS}}\) requires the knowledge of the excess free energy of the initially populated \(\sigma\pi^*\) excited state \((E_{\text{00}})\). Unfortunately, since no emission is observed from the \(\sigma\pi^*\) state of \(1^{2+}\) and the model cluster \([\text{Os}_3(\text{CO})_{10}(\text{Pr-AcPy})]\), the \(E_{\text{00}}\) value cannot be determined experimentally. The inaccessible \(\Delta G^{\circ}_{\text{CS}}\) value together with the lack of isostructural systems in which the driving force is systematically varied, prevent unravelling of the dependence of the forward and back electron transfer rates on the thermodynamic driving force. However, the large \(k_f\) value for cluster \(1^{2+}\) implies that the barrier for the forward electron transfer is relatively small. For this reason, and in analogy with the related tris(bipyridyl)ruthenium(II)-viologen systems, the forward electron transfer reaction is proposed to take place in the Marcus normal region, with the reorganization energy \(\lambda\) being close to the value of \(\Delta G^{\circ}_{\text{CS}}\). The corresponding back electron transfer is then expected to take place in the Marcus inverted region.

**Electrochemistry**

Cyclic voltammetric and IR/UV-vis spectroelectrochemical studies of the cluster \([\text{Os}_3(\text{CO})_{10}(\text{AcPy-MV}^{2+})]\) \((1^{2+})\) were performed in order to localize the reduction steps and to investigate whether the electron-trapping function of the viologen terminus may be reversibly
switched by an external potential bias. The redox potentials of cluster $1^{2+}$ and its reduction products are presented in Table 1, and the corresponding $\nu$(CO) wavenumbers in Table 2.

**Table 1.** Electrochemical data for cluster $1^{2+}$ and its reduction products.\(^{a}\)

<table>
<thead>
<tr>
<th>Cluster (^{b})</th>
<th>$E_{pc}$ [V] (^{c})</th>
<th>$\Delta E_p$ [mV] (^{d})</th>
<th>$E_{pa,a}$ [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1^{2+}$</td>
<td>-0.81 (rev)</td>
<td>90 (80)</td>
<td>+0.15 (irr)</td>
</tr>
<tr>
<td>$1^{+}$</td>
<td>-1.22 (rev)</td>
<td>90 (80)</td>
<td></td>
</tr>
<tr>
<td>$1^{-}$</td>
<td>-1.66 (rev)</td>
<td>100 (80)</td>
<td></td>
</tr>
<tr>
<td>$1^{2-}$</td>
<td>-1.92 (irr)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) Conditions and definitions: $10^{-3}$ mol dm$^{-3}$ solutions in MeCN (containing $10^{-1}$ M Bu$_4$NPF$_6$) at 293 K, unless stated otherwise; Pt disk electrode; $v = 100$ mV s$^{-1}$; redox potentials versus $E_{1/2}$(Fc/Fc$^+$); $E_{pc}$, cathodic peak potentials for reduction of parent cluster $1^{2+}$ or its reduction products; $E_{pa,a}$, anodic peak potential for oxidation of cluster $1^{2+}$; $\Delta E_p$, peak-to-peak separation for a redox couple. \(^{b}\) Assignments given in the main text. \(^{c}\) Chemical reversibility and irreversibility denoted by (rev) and (irr), respectively. \(^{d}\) $\Delta E_p$ for the Fc/Fc$^+$ internal standard in brackets.

**Figure 5.** Cyclic voltammogram of cluster $1^{2+}$ at $T = 293$ K. Conditions: $10^{-3}$ M cluster in MeCN/10$^{-1}$ M Bu$_4$NPF$_6$, Pt disk microelectrode (0.42 mm$^2$ apparent surface area), $v = 100$ mV s$^{-1}$.

The cyclic voltammogram of cluster $1^{2+}$ in MeCN shows at room temperature ($v = 100$ mV s$^{-1}$) two fully reversible reduction waves at $E_{1/2} = -0.76$ V and -1.17 V (cathodic peaks $R_1$ and $R_2$, $I_1 / I_c = 1$; see Figure 5) together with a nearly reversible one-electron reduction at $E_{1/2} = -1.60$ V (cathodic peak $R_3$, $I_a / I_c \sim 1$). In accordance with the results of IR and UV-vis spectroelectrochemical experiments (*vide infra*) and the redox potentials reported for related viologen-linked $\alpha$-diimine systems,\(^{15-18, 27}\) the first two cathodic steps represent two subsequent one-electron reductions of the viologen unit. The first one-electron step produces radical cationic cluster $1^{+}$ that is subsequently reduced at the potential $E(R_2)$ to neutral cluster $1$. Further reduction of $1$ at the potential $E(R_3)$ yields the corresponding radical anion $1^{-}$. 
Similar to the radical anions \([\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})^-]\), the unpaired electron in 1\(^-\) is most likely localized on the \(\alpha\)-diimine ligand. This conclusion is consistent with the comparable reduction potentials of the related cluster \([\text{Os}_3(\text{CO})_{10}(\text{Pr-PyCa})]\) (Pr-PyCa = \(\sigma\)-N,\(\sigma\)-N\(^\prime\)-pyridine-2-carbaldehyde-N-isopropylimine) \((E_{1/2} = -1.69 \text{ V vs } \text{Fc/Fc}^-)\) and \([\text{Os}_3(\text{CO})_{10}(\text{Pr-AcPy})]\) \((E_{1/2} = -1.76 \text{ V vs } \text{Fc/Fc}^-)\). Further evidence for this reduction pathway could be obtained from corresponding spectroelectrochemical experiments.

Figure 6. UV-vis spectral changes accompanying the first (left) and second (right) one-electron reduction step of cluster 1\(^{2+}\) in MeCN at 293 K.

The first two reduction steps of cluster 1\(^{2+}\) could indeed be conveniently followed \textit{in situ} by UV-vis spectroscopy, using an OTTLE cell. Exhaustive electrolysis at - 0.76 V in MeCN resulted in the appearance of the characteristic bands of the methylviologen radical cation (MV\(^{++}\)) that absorbs strongly at 398 nm and around 600 nm (see Figure 6). At the same time, the absorption band of MV\(^{2+}\) at 256 nm\(^{26}\) disappeared. During the subsequent reduction of 1\(^{++}\), the intense band at 398 nm slightly shifted to higher energy while its high-frequency shoulder at 376 nm increased significantly in intensity. Besides, the broad absorption band around 600 nm declined, resulting in a less intense absorption band with its maximum at 543 nm. The UV-vis spectral changes during the second reduction step are in good agreement with those observed upon one-electron reduction of free MV\(^{++}\)\(^{26}\) and are accordingly ascribed to the subsequent one-electron reduction of the viologen unit to MV\(^0\). As the latter moiety does not absorb above 500 nm\(^{26}\), the absorption band at 543 nm is ascribed to a transition possessing predominant \(\sigma(\text{Os-Os}) \rightarrow \pi^*(\alpha\text{-diimine})\) character, being slightly shifted to higher energy by \(\text{ca. } 15 \text{ nm}\) compared to the corresponding lowest-energy absorption band of non-reduced cluster 1\(^{2+}\).
Table 2. IR ν(CO) wavenumbers of cluster 1\(^{2+}\) and its reduction products.\(^{a}\)

<table>
<thead>
<tr>
<th>Cluster(^{b})</th>
<th>ν(CO) [cm(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^{2+})</td>
<td>2089 (m), 2040 (s), 2002 (vs), 1986 (s, sh), 1964 (m, sh), 1948 (m, sh), 1893 (w)</td>
</tr>
<tr>
<td>1(^{+})</td>
<td>2087 (m), 2038 (s), 1999 (vs), 1984 (s, sh), 1962 (m, sh), 1898 (w)</td>
</tr>
<tr>
<td>1</td>
<td>2085 (m), 2036 (s), 1998 (vs), 1981 (s, sh), 1959 (m, sh), 1898 (w)</td>
</tr>
<tr>
<td>1(^{-})</td>
<td>2050 (w), 2011 (m), 1972 (vs), 1952 (s, sh), 1863 (w)</td>
</tr>
</tbody>
</table>

\(^{a}\) Conditions: 10\(^{-3}\) mol dm\(^{-3}\) solutions in MeCN (containing 10\(^{-1}\) M Bu\(_4\)NPF\(_6\)) at 293 K, unless stated otherwise; \textit{in situ} reduction within an IR OTTLE cell. \(^{b}\) Assignments given in the main text.

In accordance with the UV-vis spectral changes, IR spectroelectrochemistry also proves that the first two reduction steps occur at the remote viologen unit. In particular, stepwise reduction of 1\(^{2+}\) at room temperature produces radical cation 1\(^{+}\) and neutral cluster 1 with nearly identical IR ν(CO) patterns, the bands being shifted to lower frequency by merely 2 and 4 cm\(^{-1}\), respectively, compared to the parent cluster (Figure 7). These small shifts due to a slight increase in π-backdonation towards the carbonyl ligands are consistent with the localization of the two added electrons on the remote viologen site. For, formation of radical anions [Os\(_3\)(CO)\(_{10}\)(α-diimine)]\(^{-}\) (α-diimine = \textit{e.g.} 2,2'-bipyrimidine) in which the additional electron is largely located on the α-diimine ligand, results in a more significant ν(CO) shift of \textit{ca.} 15 cm\(^{-1}\) to smaller wavenumbers compared to the parent clusters.\(^{35}\)

![Figure 7. IR spectra of 1\(^{2+}\) (-----) and the series of its one-electron reduction products 1\(^{+}\) (--), 1 (- - -) and 1\(^{-}\) (---) in MeCN at 293 K. Note that the spectrum of 1\(^{-}\) is a difference spectrum.](image)

Rapid reduction of 1 (within a minute) in the OTTLE cell also allowed spectroscopic detection of radical anion 1\(^{-}\) that is characterized by a ν(CO) pattern nearly identical to that of 1\(^{2+}\), but the ν(CO) bands being shifted by \textit{ca.} 25-30 cm\(^{-1}\) to smaller wavenumbers compared to 1. The latter shift of the ν(CO) bands closely resembles that observed upon
formation of the radical anion [Os₃(CO)₁₀(2,2'-bipyrimidine)]⁺ (vide supra) and confirms that the third electron in 1⁻ is localized on the α-diimine ligand. The thermal stability of radical anion 1⁻ at room temperature is, however, limited; it reacts further before the reduction of parent cluster 1 is completed. The IR OTTLE experiment, however, proves that radical anion 1⁻ is considerably more stable than its analogues [Os₃(CO)₁₀('Pr-PyCa)]⁻ and [Os₃(CO)₁₀('Pr-AcPy)]⁻ that are only observable within seconds at fairly low temperatures.³⁴

The results of the combined cyclic voltammetric and IR/UV-vis spectroelectrochemical study of cluster 1²⁺ clearly prove that the first two reduction steps for 1²⁺ are localized on the viologen unit. As already the first one-electron reduction of MV²⁺ significantly reduces its electron-accepting character, we investigated in the next step whether the photochemical behaviour of 1²⁺ could be controlled by an externally applied electronic bias. In order to properly address the effect of this external stimulus, the photoreactions of the clusters 1⁻ and 1⁺⁺ were studied in coordinating MeCN, the radical cation having the viologen moiety one-electron-reduced prior to photoexcitation.

**Redox-controlled photochemistry of cluster 1²⁺ in coordinating MeCN**

The photoreactivity of 1²⁺ in strongly coordinating MeCN was studied by nanosecond transient absorption (ns TA) spectroscopy. Different from acetone, the TA spectra obtained after excitation of 1²⁺ in MeCN did not indicate the presence of solvent-stabilized biradicals. Instead, strong bleaching was observed between 400 and 600 nm due to the disappearance of cluster 1²⁺, together with fairly intense transient absorption bands at 390 nm and at about 630 nm already within the laser pulse. The observed transient absorptions closely resemble those observed in the ps TA spectra of 1⁻ in acetone and are accordingly ascribed to the methyl-viologen radical cation (MV⁺⁺). This assignment implies that irradiation of 1²⁺ in MeCN results in the transfer of an electron from the cluster core to the viologen moiety. On longer time scales (up to 1 ms), however, no regeneration of the parent cluster was observed, the intensity of the absorption bands attributed to the MV⁺⁺ moiety even having increased. As the latter spectral changes most likely reflect accumulation of a long-lived photoproduct, continuous-wave (CW) irradiation experiments were performed in order to get more insight into the nature of the latter species.

Upon continuous-wave irradiation with the 514.5 nm line of an argon-ion laser, cluster 1²⁺ transformed into a blue-coloured photoproduct, possessing IR ν(CO) bands at 2137 (w), 2123 (w), 2083 (w), 2071 (sh), 2053 (m), 2020 (vs), 1990 (s), 1956 (w) and 1932 (w) cm⁻¹. The IR ν(CO) spectral changes following this photoreaction are shown in Figure 8. It is noteworthy that the photoproduct is fairly stable at room temperature and could be formed in relatively high yields (up to 85%).
Figure 8. IR spectral changes accompanying photolysis of cluster \( \text{I}^{2+} \) in MeCN at 293 K (\( \lambda_{\text{ir}} = 514.5 \) nm). Inset: IR spectrum obtained upon photooxidation of \( \text{I}^{2+} \) (A) and electrochemical oxidation (B) of \([\text{Os}_3(\text{CO})_{10}(\text{Pr-AcPy})]\) in a thin-layer electrochemical cell.

The shift of the v(CO) bands to much larger wavenumbers compared to \( \text{I}^{2+} \) points to a significant decrease in \( \pi \)-backbonding towards the carbonyl ligands and is consistent with the formal one-electron photooxidation of the cluster core. In fact, the above v(CO) pattern (Figure 8, inset A) closely resembles that obtained separately by irreversible electrochemical oxidation of the related cluster \([\text{Os}_3(\text{CO})_{10}(\text{Pr-AcPy})]\) in MeCN (\( E_{\text{p,a}} = +0.16 \) V) (Figure 8, inset B). Although research is in progress to assign the product(s) of the latter oxidation, a preliminary spectroelectrochemical study of a series of clusters \([\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})]\) revealed that the shift of the v(CO) bands to larger wavenumbers upon oxidation is dependent on the \( \alpha \)-diimine ligand used. Notably, reverse reduction of the oxidation product\(^\dagger\) of \([\text{Os}_3(\text{CO})_{10}(\text{Pr-AcPy})]\) in MeCN results in the nearly complete regeneration of the parent cluster. These results indicate that upon oxidation the clusters \([\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})]\) most likely undergo a reversible structural change, with the \( \alpha \)-diimine ligand coordination retained.

Based on the results of the continuous-wave experiments and the observation of the transient bands characteristic for MV\(^{\text{II}}\) in the ns TA spectra of \( \text{I}^{2+} \) in MeCN, the blue-coloured photoproduct is proposed to result from a similar electron transfer reaction as observed in acetone, with one electron being transferred from the cluster core to the viologen moiety. In contrast with the results in acetone, however, the photoproduct in MeCN does not regenerate the parent cluster on the time scale of minutes. This clearly reflects the influence of the strongly coordinating solvent that stabilizes the photooxidized cluster core, thereby significantly retarding the thermal back electron transfer.

\(^\dagger\) In fact, the oxidation product consists of a mixture of at least two different species, the ratio being dependent on the solvent and oxidation method applied (bulk electrolysis, thin-layer electrolysis, chemical oxidation, etc.).
In order to investigate whether the electrochemical one-electron reduction of the viologen moiety of $1^{2+}$ is capable of switching its electron-trapping character, we focused in a next step on the photochemical behaviour of the radical $1^{-}$. As CW irradiation in MeCN did not induce any significant photochemical reactivity, the photoreactions of $1^{-}$ were followed with rapid-scan FTIR spectroscopy in the (sub)second time domain. After in situ reduction of $1^{2+}$ in an OTTLE cell, cluster $1^{-}$ was irradiated with a short CW laser pulse of an argon-ion laser (488 nm, 300 mW, 4 s) and the IR spectral changes in the CO-stretching region were monitored on the time scale of seconds to minutes. The difference IR spectra of $1^{-}$ in MeCN, measured 0-6 s after the laser pulse are depicted in Figure 9.

The difference IR spectra recorded directly after the photoexcitation of $1^{-}$ display instantaneous bleaching of the parent $v$(CO) bands together with two transient bands at 1970 (s) and 1873 (m, br) cm$^{-1}$. Both the transient absorptions and the parent bleaches decay with a lifetime of ca. 6 s, upon almost complete regeneration of the parent cluster. The observed transient absorption bands closely resemble those observed upon irradiation of [Os$_3$(CO)$_{10}$'Pr-AcPy)] in MeCN (see Chapter 4, part A) and are accordingly ascribed to the solvent-stabilized zwitterion ["Os(CO)$_4$-Os(CO)$_4$-"Os(S)(CO)$_2$(AcPy-MV$^*$)] (S = MeCN). The formation of zwitterions upon irradiation of $1^{-}$ is indicative of a greatly diminished driving force for the oxidative quenching of the $\sigma\pi^*$ excited state by the reduced viologen moiety. In contrast to the results for $1^{2+}$, the photoinduced electron transfer to the latter unit is therefore no longer feasible. Instead, one-electron reduction of the viologen unit restores the 'original' photochemical behaviour observed for the reference cluster [Os$_3$(CO)$_{10}$'Pr-AcPy)]. The lifetime of the zwitterion formed upon irradiation of $1^{-}$ (6 s) is, however, significantly reduced compared to that of its unsubstituted counterpart lacking the electron-accepting moiety (38 s). This difference cannot be explained by electronic reasons, as [Os$_3$(CO)$_{10}$($\alpha$-diimine)] clusters produce longer-lived zwitterions for more electron-accepting $\alpha$-diimines (2,2'-bipyridimide: $\tau = 9.0$ s in MeCN) compared to stronger donors (2,2'-bipyridine: $\tau = 5.6$ s in MeCN). In the case of $1^{-}$ the reduced zwitterion lifetime is therefore likely due to steric hindrance of the methylviologen side-arm. Most importantly, the rapid scan results show that the photochemical behaviour of $1^{2+}$ changes upon the one-electron reduction of the viologen unit and may indeed be controlled by applying an external potential bias. Similar changes in the photochemical or photophysical behaviour upon reduction of a remote electron-acceptor unit have been observed for Ru(bpy)$_3$-acceptor dyads bearing reversibly reducible viologen or $p$-quinone units. For example, the quenching of the emitting $^3$MLCT excited state of a Ru(bpy)$_3$-MV$^{2+}$ dyad, where the viologen moiety is covalently attached to the 4-position of one of the bipyridine ligands, changes from oxidative to reductive upon one-electron reduction of the MV$^{2+}$ unit.
Redox-Controlled Charge-Transfer Photochemistry of \([\text{Os}_3(\text{CO})_{10}(\text{AcPy-MV}^\text{V})]\)

Figure 9. Difference rapid scan IR spectra of one-electron-reduced cluster \(1^{+}\) in MeCN, measured at time delays of 1, 2, 4 and 6 s after the 488.0 nm laser pulse.

Based on the observed differences in the photochemical behaviour of clusters \(1^{2+}\) and \(1^{+}\), the \([\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})]\)-viologen (donor-acceptor) dyad can be designated as a molecular redox switch. In this system the \(\text{Os}_3/\alpha\text{-diimine}\) core acts as the photoactive centre (chromophore), while the methylviologen fulfills the requirements of a bistable switching element, controlled by an external stimulus. The implementation of the reversible MV\(^{2+}/MV^{+}\) redox couple into cluster \(1^{2+}\) may therefore allow the direction of electron transfer and the concomitant structural change upon light excitation to be controlled by the state of the switchable unit. In practice, both the reduced (\(1^{+}\)) and oxidized (\(1^{2+}\)) forms of the switch are stable in MeCN but the reversibility is lost upon irradiation of \(1^{2+}\). Photoinduced charge-separation in this case results in trapping of the system in a 'locked' state, which may be unlocked electrochemically (\textit{vide infra}).

Summarizing the redox-controlled photochemistry of \(1^{2+}\) in MeCN (Scheme 5), irradiation of the reduced form (\(1^{+}\)) results in splitting of an Os-Os(\(\alpha\)-diimine) bond and ultimate formation of open-structure zwitterions, which were detected by rapid scan FTIR spectroscopy. As the structural change upon zwitterion formation is completely reversible, the read-out of the reduced state is non-destructive and completely regenerates cluster \(1^{+}\). Upon irradiation of the oxidized form (\(1^{2+}\)) rapid electron transfer to the remote viologen site is observed, resulting in photooxidation of the cluster core. Notably, the latter process shows close correspondence with the irreversible electrochemical oxidation of \([\text{Os}_3(\text{CO})_{10}(\text{Pr-AcPy})]\). Indeed, the formation of the charge-separated photoproduct does not result in thermal regeneration of the parent cluster. However, as back reduction of the electrochemically oxidized product at a more negative potential results in nearly complete regeneration of the parent cluster (\textit{vide supra}), the structural change upon irradiation of \(1^{2+}\) is also expected to be
chemically reversible. By applying an external potential in between the back reduction of the oxidized cluster core and the oxidation of MV\(^{**}\) (O\(_1\)) (see Figure 5), the complete recovery of 1\(^{2+}\) may be established \textit{via} electrode-mediated back electron transfer. In this way, the redox switch may be reset to its original state.

Scheme 5. Redox-controlled photochemistry of cluster 1\(^{2+}\) in MeCN (Sv).

The thermally irreversible photoreaction upon irradiation of 1\(^{2+}\) in MeCN makes the latter solvent, however, less attractive for the clear-cut application of the Os\(_3/\alpha\)-diimine-viologen dyad as a reversible redox switch. Strongly coordinating MeCN was initially selected for this study as the zwitterionic photoproducts formed upon irradiation of 1\(^{+}\) in this solvent are easily detectable by rapid scan FTIR spectroscopy. In contrast to the results in MeCN, irradiation of 1\(^{2+}\) in acetone gives rise to a fast and \textit{reversible} electron-transfer reaction (\textit{vide supra}). Experiments are therefore in progress to prove the stability of one-electron-reduced 1\(^{+}\) also in the latter solvent. If true, irradiation of 1\(^{+}\) in acetone will result in the formation of solvent-stabilized biradicals, detectable by nanosecond transient absorption spectroscopy. As the latter biradicals are known to regenerate the parent cluster (see Part B), the use of acetone as a solvent may result in completely reversible photochemistry for both the oxidized and reduced forms of the molecular switch.
4C.5 Conclusions

Transient absorption and time-resolved IR spectroscopies on the picosecond time scale document that irradiation of cluster $1^{2+}$ in acetone results in the formation of a charge-separated (CS) state with an electron transferred from the cluster core to the remote viologen unit. The CS state proved to be populated via fast (4.4 x 10$^{11}$ s$^{-1}$) and efficient (> 92%) oxidative quenching of the initially populated $\sigma\pi^*$ excited state and decays bi-exponentially, upon nearly complete regeneration of the parent cluster, with lifetimes of 43 and 180 picoseconds (3:2 ratio).

The direction of the electron transfer and the concomitant structural change upon light excitation can be controlled by the redox state of the viologen moiety. Irradiation of $1^{2+}$ in acetonitrile results in the formation of a stable photoproduct via a similar electron transfer process as studied in acetone. One-electron reduction of the viologen unit then reduces its electron-accepting character to such an extent that the photoinduced electron transfer to the latter unit is no longer feasible. Instead, irradiation of $1^+$ results in the formation of zwitterions, the common photoproducts for the clusters [Os$_3$(CO)$_{10}$($\alpha$-diimine)] in strongly coordinating solvents.

In general, the thorough understanding of the electron transfer reactions of the cluster [Os$_3$(CO)$_{10}$($\text{Pr-AcPy}$)] has allowed us to realize a purpose-designed [Os$_3$(CO)$_{10}$($\alpha$-diimine)]-MV$^{2+}$ (donor-acceptor) dyad that, consistent with its photochemical behaviour in MeCN, can be designated as a molecular redox switch. The principle of controlling the direction of electron transfer by the redox state of the switchable element may be extended, allowing selective communication between the chromophore with two different acceptor termini. The creation of such (supra)molecular systems capable of signal generation and selective transfer is not only challenging but may also find important applications in the field of molecular nanoelectronics.

4C.6 References

Chapter 4. Part C


Redox-Controlled Charge-Transfer Photochemistry of \([\text{Os}_2(\text{CO})_{10}(\text{AcPy-MV}^2)^-]\)


