Novel Complexes *trans*(Cl)-[Os(bpy)(CO)(CH_3CN)Cl_2]^n (n = 0, +1; bpy = 2,2′-Bipyridine): Photo- and Electrochemical Syntheses and Comparative Study of Their Bonding and Redox Properties

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Photoirradiation of the complex *trans*(Cl)-[Os(bpy)($CO)_2Cl_2$] in acetonitrile with $\lambda \geq 320$ nm light gives rise to substitution of a CO ligand, with the formation of *trans*(Cl)-[Os(bpy)-(CO)(CH_3CN)Cl_2]. The bonding properties and redox reactions of the novel photoproduct were thoroughly investigated by several methods such as nanosecond time-resolved UV/Vis absorption and resonance Raman spectroscopy, cyclic voltammetry, and IR and UV/Vis spectroelectrochemistry. Its one-electron electrochemical oxidation in acetonitrile produces the stable cation *trans*(Cl)-[Os(bpy)(CO)(CH_3CN)Cl_2]$^+$. This complex is also formed as the major product during one-electron oxidation of the dicarbonyl precursor *trans*(Cl)-[Os(bpy)($CO)_2Cl_2$] in acetonitrile at room temperature. By contrast, the initial dicarbonyl oxidation product *trans*(Cl)-[Os(bpy)($CO)_2Cl_2$]$^+$ remains stable in dry noncoordinating dichloromethane and in butyronitrile at low temperatures. The CO-loss reactivity of *trans*(Cl)-[Os(bpy)($CO)_2Cl_2$], induced by the partial oxidation of the formally osmium(II) centre, is dramatically lower compared to the corresponding ruthenium(II) complex due to the stronger Os–CO bonds. Replacement of one CO or Cl ligand in *trans*(Cl)-[Os(bpy)-($CO)_2Cl_2$] by a stronger σ-donor CH_3CN or isopropoxycarbonyl [–C(O)O*i*Pr] ligands strengthens the Os–CO bond(s) and results in photostable derivatives.

Introduction

In the past two decades considerable attention has been paid to the synthesis,[1−3] electrochemistry,[4−6] photochemistry[7−10] and (photo-, electro-)catalytic properties[11−17] of the complex *trans*(Cl)-[Ru(bpy)($CO)_2Cl_2$] (bpy = 2,2′-bipyridine) and its derivatives. The active species in the electrocatalytic reduction of CO_2 with this complex is the insoluble polymer [Ru(bpy)($CO)_2$]$_n$ resulting from a two-electron reduction pathway. Its physicochemical properties and reactivity can be finely tuned by attachment of different substituents at the bpy rings.[5] We have been particularly interested whether a major difference in this regard can be achieved by replacement of the ruthenium centre by the heavier osmium. In general, osmium complexes are less reactive and therefore better suited for mechanistic studies. The properties of the corresponding precursor osmium complex *trans*(Cl)-[Os(bpy)($CO)_2Cl_2$] (**1**) have been relatively unexplored. Apart from its synthesis and brief spectroscopic characterisation,[18] only a preliminary electrochemical study has recently been reported.[19] In addition, an analogous complex **1a** with 4,4′-dimethyl-2,2′-bipyridine (dmb) was prepared as a precursor of the luminescent complex *trans*($SnPh_3$)-[Os(dmb)($CO)_2$($SnPh_3$)$_2$].[20−22] As a part of our continued studies of bonding properties and reactivity of complex **1** and its derivatives, we describe in the present work its charge-transfer photochemical reactivity [Equation (1)] and electrochemical oxidation [Equation (2)], both promoting CO substitution reaction by the donor solvent acetonitrile. The studied osmium complexes will also be compared with the corresponding ruthenium compounds.

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$$[Os(bpy)(CO)_2Cl_2] \xrightarrow[CH_3CN]{h\nu} [Os(bpy)(CO)(CH_3CN)Cl_2] + CO \quad (1)$$

$$[Os(bpy)(CO)_2Cl_2] \xrightarrow[CH_3CN]{-e^-} [Os(bpy)(CO)(CH_3CN)Cl_2]^+ + CO \quad (2)$$

Results and Discussion

Photochemical Formation and Characterization of [Os(bpy)(CO)(CH_3CN)Cl_2] (2)

Irradiation of *trans*(Cl)-[Os(bpy)(CO)$_2$Cl$_2$] (**1**) in CH_3CN with a 250-W Xe lamp into its predominantly Os-to-bpy charge transfer band at 364 nm produces within a few hours exclusively the photostable monocarbonyl complex *trans*(Cl)-[Os(bpy)(CO)(CH_3CN)Cl_2] (**2**) (Figure 1). The composition of the photoproduct has been verified by mass spectrometry and elemental analysis. Its *trans*(Cl) geometry can be deduced from the corresponding ^{1}H NMR spectrum, in particular from the coinciding signals of the 2,2′-bipyridine hydrogen atoms 6-H and 6′-H at δ = 9.05 ppm (see Scheme 1 and Exp. Sect.).[23] The identity of complex **2** has further been confirmed by IR spectroscopy. During the irradiation, the two ν(CO) bands of the parent complex **1** (2038 and 1968 cm^{-1}; CH_3CN) are replaced by a single band at 1933 cm^{-1}. Such a large wavenumber drop is quite normal for CO substitution in a dicarbonyl complex, resulting in considerably increased π-back-bonding to the remaining CO ligand. For comparison, a similar situation applies for *cis*(Cl)-[Ru(bpy)(CO)$_2$Cl$_2$] [ν(CO) at 2067 and 2001 cm^{-1}; CH_3CN] and *cis*(Cl)-[Ru(bpy)(CO)(CH_3CN)Cl_2] [ν(CO) at 1969 cm^{-1}; CH_3CN].[9] The typically smaller ν(CO) wavenumbers for the osmium(II) compounds compared to their ruthenium(II) derivatives [$\Delta\nu$(CO) $\approx$ 30 cm^{-1} for corresponding bands] reflect the stronger bond between CO and the 5d metal atom.

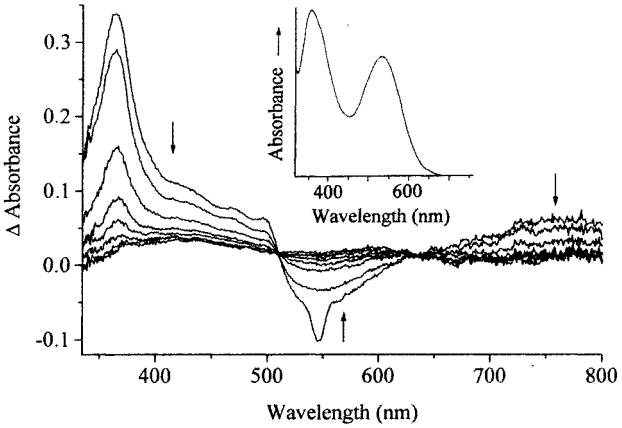
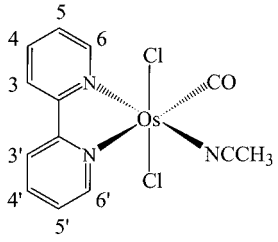


Figure 1. Nanosecond TA spectra of complex **2** in acetonitrile (λ_{exc} = 545 nm, time increment 5 ns, 50 accumulations); the MLCT/XLCT (X = Cl; L = 2,2-bipyridine) excited-state lifetime τ = 12.6 ns at 293 K; inset: UV/Vis spectrum of complex **2** in acetonitrile



Scheme 1. Schematic molecular structure of complex **2** with numbering of 2,2′-bipyridine proton nuclei for assignment of ^{1}H NMR signals

In the course of the photoreaction the initially yellow solution of **1** (λ_{max} = 364 nm in acetonitrile) turns progressively purple due to the appearance of a new visible absorption band of complex **2** at λ_{max} = 535 nm; in addition, a new band also grows at 362 nm (Figure 1, in set). This spectral change is consistent with a significantly higher energy of the largely d_π(Os)-centred highest occupied molecular orbital (HOMO) of complex **2** compared to that of precursor **1**. The higher energy of the HOMO is evidenced by the much less positive $E_{1/2}(Os^{II}/Os^{III})$ oxidation potential for **2** (see below), reflecting sensitively the substitution of the π-acceptor carbonyl ligand by the stronger σ-donor acetonitrile ligand. On the other hand, the lowest unoccupied π^* (bpy) orbital (LUMO) rises by much less energy upon the photosubstitution than the HOMO, as can be concluded from the close $E_{1/2}$(bpy/bpy$^{\cdot-}$) reduction potentials for **1** and **2** (see below).

In order to assign the lowest-energy electronic transition of complex **2**, nanosecond time-resolved absorption (TA) spectra (Figure 1) and resonance Raman spectra (Figure 2) were recorded upon irradiation into the visible absorption band at 535 nm. The difference UV/Vis absorption spectra in Figure 1 show a bleaching between 500 and 630 nm due to the disappearance of complex **2** (inset to Figure 1) that completely regenerates in 35 ns after the laser pulse. The transient absorption between 630 and 800 nm can be ascribed to the lowest π^*-π^* transitions of the aromatic [bpy]$^{\cdot-}$ ligand;[24] another set of π^*-π^* transitions is observed as a band with two characteristic absorption maxima at 467 and 497 nm. The strong transient band at 363 nm probably belongs to the π-π^* transition of [bpy]$^{\cdot-}$. The shoulder at 418 nm may reflect the presence of the formally Os^{III} centre in the excited transient, as a similar absorption band appears in the UV/Vis spectrum of the electrochemically one-electron-oxidised Os^{III} species **2**$^+$ (see below and Figure 3). The TA data thus indicate that the lowest optically accessible excited state has an osmium(II)-to-bpy charge-transfer (MLCT) character. On the other hand, resonance Raman spectra of nonluminescent **2**, dispersed in KNO_3 and irradiated with 514.5 nm (Figure 2) and 543 nm light, show only a weak rR effect of ν_s(CO) at 1917 cm^{-1}. [For comparison, the ν(CO) band of complex **2**, dispersed in KBr, occurs at 1927 cm^{-1}, i.e. lower by 6 cm^{-1} than found in acetonitrile, see above]. This implies that the Os-to-CO π-back-bonding is not strongly affected by this electronic transition. Characteristic resonance-enhanced Raman bands of the bpy ligand are found at 1606, 1557 [both ν(C=C)], 1493, 1325 [both ν(C=N)], 1278 [ν(C−C) inter-ring], 1177 [δ(CCH) in-plane], 1031 (ring breathing) and 669 [δ(CCC) inter-ring] cm^{-1}. Importantly, an apparent Raman band due to ν_s(Os−Cl) is observed at 302 cm^{-1}, consistent with a relatively strong rR effect on the Os−Cl bonds. However, the overall rR effect is rather weak and,

hence, the normal coordinates of complex **2** are less affected by the electron transfer to π*(bpy) than would be expected for an MLCT transition. Instead, the rR spectra of complex **2** agree with a mixed MLCT/XLCT (X = Cl) character of the lowest optically accessible excited state. Its lifetime τ = 12.6 ns at 293 K has been determined from the TA data (see above).

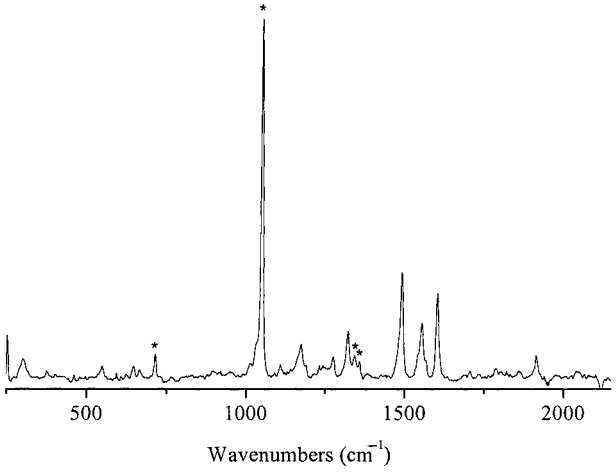


Figure 2. Resonance Raman spectrum of complex **2** dispersed in a KNO_3 pellet; λ_{exc} = 514.5 nm; bands due to KNO_3 indicated by an asterisk

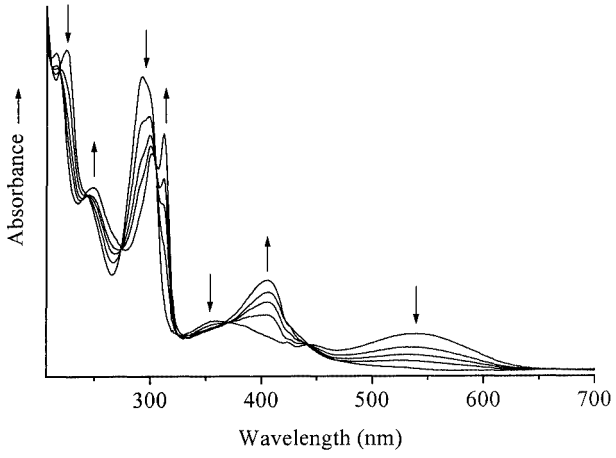


Figure 3. UV/Vis spectral changes recorded during the one-electron oxidation of complex **2** (10^{-3} M) in acetonitrile; electrolysis within an OTTLE cell[38] at 293 K

Unfortunately, the CO-loss photoreactivity and luminescence of complex **1** prevented the recording of both TA and resonance Raman spectra for this complex and comparison with complex **2**.

A similar difference in the CO-loss reactivity was also observed between the corresponding cations $\mathbf{1}^+$ and $\mathbf{2}^+$ produced by electrochemical oxidation (see below). This observation is consistent with removal of electron density from the highest occupied molecular orbital, similarly to the situation in the mixed lowest-energy charge-transfer excited state of the Os^{II} complexes **2**. The cyclic voltammogram (CV) of the photoproduct **2** dissolved in $CH_3CN/10^{-1}$ M TBAP indeed shows a completely reversible Os^{II}/Os^{III} redox couple at $E_{1/2}$ = 0.45 V vs. Ag/Ag^+ that is positioned less positively by 0.80 V than the one-electron oxidation of parent complex **1**.[19] This observation agrees with the strong σ-donor ability of the CH_3CN ligand compared to the expulsed π-acceptor carbonyl ligand, thereby stabilizing the formal osmium(III) oxidation state in $\mathbf{2}^+$. Exhaustive oxidation of complex **2** at 0.55 V upon bulk electrolysis or within a thin-layer spectroelectrochemical cell produced the corresponding inherently stable cation $\mathbf{2}^+$ quantitatively. The UV/Vis spectrum of the oxidised product exhibits a low-energy absorption band at 406 nm (ε_{max} = 5500 M^{-1} cm^{-1}) tailing down to 550 nm. The UV/Vis spectral changes accompanying the formation of $\mathbf{2}^+$ within an OTTLE cell are shown in Figure 3. In the infrared region the single ν(CO) band of $\mathbf{2}^+$ (2047 cm^{-1}) is shifted to larger wavenumbers by 114 cm^{-1} compared to parent complex **2** (1933 cm^{-1}). The large ν(CO) difference testifies to the predominantly Os-localised oxidation, resulting in strongly diminished Os-to-CO π-back-bonding.[25]

Unlike the completely irreversible reduction of the dicarbonyl precursor **1** in CH_3CN electrolyte at room temperature and moderate cyclic voltammetric scan rates,[19] complex **2** is reduced under the same experimental conditions in a nearly chemically reversible one-electron step at $E_{1/2}$ = −1.80 V (I_{pa}/I_{pc} = 0.93 at v = 100 mV s^{-1}). As mentioned above, the π*(bpy) LUMO energy for complex **2** is slightly higher than complex **1**, which is reversibly reduced at a less negative potential: $E_{1/2}$ −1.64 V (THF, 293 K)[19] and −1.62 V (PrCN, 273 K). Exhaustive electrolysis of **2** in acetonitrile at −1.90 V leads to the formation of a dark film, weakly adherent to the working electrode surface, together with a green solution containing 1 mol-equiv. of free chloride ions, as revealed by voltammetry on a rotating disk electrode.[29] In situ IR spectroelectrochemical study of this cathodic process in acetonitrile/10^{-1} M TBAP at room temperature showed disappearance of the ν(CO) band of **2** at 1933 cm^{-1} and formation of a new reduced complex **2R**, absorbing at 1890 cm^{-1}. The parallel thin-layer cyclic voltammetric scan shows that **2R** is not the one-electron-reduced radical anion $\mathbf{2}^{\cdot-}$ [stable in PrCN at 253 K, ν(CO) at 1895 cm^{-1}], as its reverse oxidation occur 0.45 V less negatively than the initial reduction of precursor **2**. Further reduction of **2R** is chemically reversible ($E_{1/2}$ = −1.96 V), causing a shift of the ν(CO) band to 1857 cm^{-1}. This behaviour of complex **2** upon reduction closely resembles that of complex **1**,[19] pointing to the formation of an Os−Os-bonded species. Detailed experimental studies of the reduction paths of complexes **1** and **2** are in progress and will be published in a separate paper.

Electrochemical Formation of [Os(bpy)(CO)(CH_3CN)Cl_2] (2)

Electrochemical oxidation of complex **1** to the formally osmium(III) species $\mathbf{1}^+$ ($E_{1/2}$ = 1.23 V vs. Ag/Ag^+ in acetonitrile[19]) is completely reversible on the time scale of cyclic voltammetry at room temperature, independently of the solvent used {acetonitrile [see Figure 4 (a)], butyronitrile, dichloromethane}. The less positive oxidation potential

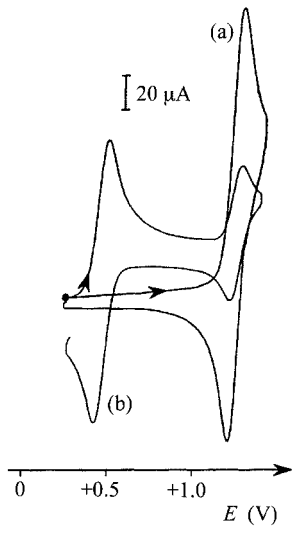


Figure 4. Cyclic voltammograms recorded (a) before and (b) after exhaustive one-electron oxidation of complex **1** (2.71×10^{-3} M) at 1.35 V and subsequent back reduction of the oxidised species $\mathbf{1}^+$ and $\mathbf{2}^+$ at 0.25 V at a Pt sheet electrode; conditions: acetonitrile containing 10^{-1} M TBAP and 1 μL of H_2O per 10 mL of CH_3CN, Pt disk electrode (5 mm diameter), scan rate 100 mV s^{-1}, T = 293 K

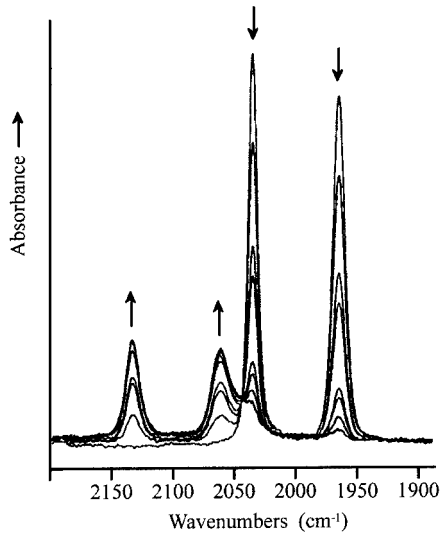


Figure 5. Spectral changes in the IR ν(CO) region recorded during the reversible oxidation of complex **1** (ca. 5×10^{-3} M) to $\mathbf{1}^+$ in butyronitrile; electrolysis within an OTTLE cell[39] at 273 K

of complex **1** compared to *trans*(Cl)-[Ru(bpy)($CO)_2Cl_2$] ($E_{1/2}$ = 1.45 V vs. Ag/Ag^+)[4,5] is generally encountered also for other types of Ru^{II} and Os^{II} complexes, such as classical $[M(bpy)_3]^{2+}$ (M = Ru, Os) and their numerous derivatives.[30] Bulk electrolysis of **1** at +1.35 V, carried out in acetonitrile containing a small amount of water (0.01%),[4] produced a mixture of $\mathbf{1}^+$ and $\mathbf{2}^+$ in 30% and 70% yield, respectively. Their quantitative back reduction at 0.25 V gave the corresponding neutral complexes **1** and **2** that were analysed by cyclic voltammetry [Figure 4 (b)]. Notably, both cations $\mathbf{1}^+$ and $\mathbf{2}^+$ are unstable during the bulk electrolysis in dry acetonitrile.

On the other hand, cation $\mathbf{1}^+$ could be completely stabilised in dry noncoordinating dichloromethane (at 293 K) or in dry butyronitrile electrolyte (at 273 K). The corresponding IR spectroelectrochemical studies showed the complete conversion of **1** [ν(CO) at 2037, 1967 cm^{-1} in dichloromethane (293 K); 2036, 1966 cm^{-1} in butyronitrile (273 K)], into $\mathbf{1}^+$ [ν(CO) at 2129 and 2056 cm^{-1} in dichloromethane (293 K); 2144 and 2063 cm^{-1} in butyronitrile (273 K)]. Notably, the ν(CO) bands of the cationic product $\mathbf{1}^+$ possess much lower intensity than those of the parent complex (see Figure 5). The large CO-stretching wavenumbers for $\mathbf{1}^+$ again imply one-electron oxidation predominantly localised on the osmium centre.[25] The UV/Vis spectrum of $\mathbf{1}^+$ in dichloromethane is very similar to that of the electrochemically oxidised photoproduct $\mathbf{2}^+$ in acetonitrile (see Figure 3), the maximum of the new lowest-lying absorption band of $\mathbf{1}^+$ being merely shifted to 385 nm. Apparently, the corresponding electronic transition in the formally osmium(III) complexes $\mathbf{1}^+$ and $\mathbf{2}^+$ with *trans*(Cl) geometry is not much affected by the substitution of the CO ligand by acetonitrile. Its assignment, however, has not been attempted, as support from theoretical MO studies is needed for a precise description of the molecular orbitals involved.

In contrast, when the butyronitrile electrolyte is replaced with acetonitrile, the oxidation of complex **1** within the IR OTTLE cell at 273 K produces besides $\mathbf{1}^+$ [ν(CO) at 2135, 2063 cm^{-1}] also CO-substituted $\mathbf{2}^+$ [ν(CO) at 2048 cm^{-1}] as the minor secondary product ($\mathbf{1}^+/\mathbf{2}^+ \approx 3:1$). At room temperature $\mathbf{2}^+$ becomes the major product ($\mathbf{1}^+/\mathbf{2}^+ \approx 1:4$). When the one-electron oxidation of complex **1** is nearly completed, two additional secondary products begin to form both at 293 and 273 K. At the same time the concentrations of $\mathbf{1}^+$ and $\mathbf{2}^+$ decrease. These cations are apparently in equilibrium. One of the ultimate products can be assigned as $[Os^{II}(bpy)(CO)_2(CH_3CN)Cl]^+$ [ν(CO) at 2066 and 2003 cm^{-1}], based on the comparison with $[Ru^{II}(bpy)(CO)_2(CH_3CN)Cl]^+$ [ν(CO) at 2091 and 2035 cm^{-1}][31] and taking into account the likely ν(CO) wavenumber difference of ca. 30 cm^{-1} (see above). The other tertiary product [ν(CO) at 2058 and 1991 cm^{-1}] has remained unassigned. Possibly, two different structural isomers of $[Os^{II}(bpy)(CO)_2(CH_3CN)Cl]^+$ are formed in similar amounts. As a plausible explanation of the observed anodic behavior, CO liberated during the formation of $\mathbf{2}^+$ cannot escape from the thin electrolyte layer within the spectroelectrochemical cell and remains dissolved in the vicinity of the working electrode. At the end of the electrolysis the CO concentration increased sufficiently to trigger the reaction with cations $\mathbf{1}^+$ or $\mathbf{2}^+$ and the replacement of one chloride ligand with the formation of $[Os^{III}(bpy)(CO)_2(CH_3CN)Cl]^{2+}$. Importantly, the thin-layer cyclic voltammetric scan recorded during the oxidation of complex **1,** has proven that $[Os^{II}(bpy)(CO)_2(CH_3CN)Cl]^+$ is not further oxidised to the corresponding dication before the anodic limit of the potential "window" of the acetonitrile electrolyte is reached. The generation of the oxidised transient $[Os^{III}(bpy)(CO)_2(CH_3CN)Cl]^{2+}$ from complex $\mathbf{2}^+$, even though inefficient,

must therefore be coupled to its instantaneous one-electron reduction at the applied electrode potential of the **1/1**$^+$ redox couple, resulting in the stable complex $[Os^{II}(bpy)(CO)_2(CH_3CN)Cl]^+$. In this way $[Os^{II}(bpy)(CO)_2(CH_3CN)Cl]^+$ is formed at the expense of **1**$^+$ and **2**$^+$ until the process becomes inhibited owing to decreased CO concentration.

Comparison of the CO-Loss Reactivity of Complexes $[M(bpy)(CO)_n(CH_3CN)_{2-n}Cl_2]$ (M = Ru, Os; n = 1, 2)

It is important to recall that electrochemical oxidation of the complex *trans*(Cl)-$[Ru(bpy)(CO)_2Cl_2]$ in acetonitrile, containing a small amount of water, induces decoordination of one CO and one Cl ligand, producing the Ru^{III} complex $[Ru(bpy)(CO)(CH_3CN)_2Cl]^{2+}$. The completely decarbonylated Ru^{III} compound $[Ru(bpy)(CH_3CN)_2Cl_2]^{2+}$ is also formed in low yield (5%) in this medium.[4] In contrast to this, for the corresponding Os^{II} complex **1** it proved possible to substitute merely a single CO ligand, by electrochemical one-electron oxidation producing the cationic species **2**$^+$. Moreover, the CO substitution is incomplete even in aqueous CH_3CN electrolyte at ambient temperature and a mixture of cations **1**$^+$ and **2**$^+$ is produced. Substitution of a chloride ligand in the course of the oxidation of complex **1**, producing ultimately the Os^{II} complex $[Os(bpy)(CO)_2(CH_3CN)Cl]^+$, could only be achieved under special conditions of locally increased CO concentration in the acetonitrile electrolyte. These results point to much stronger Os−CO bonds in complex **1**$^+$, but also in **2**$^+$, compared to the corresponding ruthenium derivatives. This conclusion is supported by the lower ν(CO) frequencies for the Os^{II} complexes (see above). The σ,π-donation from the chloride ligands is assumed to play an important role in the stabilization of the formal metal(III) oxidation state, strengthening the metal-to-CO π-backbonding and, hence, the metal(III)−CO bonds. A comparison of ν(CO) frequencies for the corresponding Os^{III} and Ru^{III} complexes would be useful in this regard. Unfortunately, the oxidised Ru^{III} complexes *trans*(Cl)-$[Ru(bpy)(CO)_2Cl_2]^+$ and $[Ru(bpy)(CO)(CH_3CN)Cl_2]^+$ have not been characterised so far by IR spectroscopy.

Similar arguments can be used to explain the relatively slow dissociative photosubstitution reaction of complex **1** in acetonitrile, producing the monocarbonyl complex *trans*(Cl)-$[Os(bpy)(CO)(CH_3CN)Cl_2]$ (**2**). Resonance Raman spectra of the latter photostable complex have shown that its lowest-energy optically populated excited state has a mixed MLCT/XLCT character. This unreactive excited state apparently does not interact with any reactive state from which a CO-loss reaction would occur [e.g. ligand-field (LF) or metal-to-CO charge-transfer (MLCT) states[10,32]. In contrast to this, the related 4d-ruthenium complex *cis*(Cl)-$[Ru(bpy)(CO)(CH_3CN)Cl_2]$ is readily photoreactive and converts into $[Ru(bpy)(CH_3CN)_2Cl_2]$.[7] Time-resolved spectroscopic studies and theoretical MO calculations are needed to describe the reactive (dissociative) state in the latter case.

Time-dependent DFT calculations on the complex *trans*(Cl)-$[Ru(Me\text{-}DAB)(CO)_2Cl_2]$ (Me-DAB = *N*,*N*′-dimethyl-1,4-diaza-1,3-butadiene) have revealed a mixed XLCT/MLCT character of its lowest-energy allowed electronic transition, while CASSCF/CASPT2 ab initio calculations favour its predominant MLCT assignment.[33] The CO-loss reactions of the analogous ruthenium complex *trans*(Cl)-$[Ru(bpy)(CO)_2Cl_2]$ and the studied complex **1** probably occur upon optical preparation of a similar Franck-Condon excited state. Upon light absorption and electron transfer to the π*(bpy) orbital the metal centre becomes partly oxidised, resulting in diminished π-backbonding toward the CO ligands bound in the equatorial metal−bpy plane. The stabilization of the metal−CO bonds by increased donation of electron density to the $M(CO)_2$ unit from the axial donor ligands plays a crucial role in tuning the photoreactivity. Thus, incorporation of a stronger σ-donor isopropoxycarbonyl [−C(O)O*i*Pr] ligand instead of chloride results in a photostable complex $[Os(bpy)(CO)_2\{C(O)OiPr\}Cl]$.[34] Under identical experimental conditions, the isomeric ruthenium(II) photoproduct *cis*(Cl)-$[Ru(bpy)(CO)(CH_3CN)Cl_2]$ is formed from *trans*(Cl)-$[Ru(bpy)(CO)_2Cl_2]$ markedly more rapidly (within a few minutes),[7,9] again consistent with weaker Ru−CO bonds in the reactive excited state and in analogy with the electrochemical oxidation. It is also possible that for the less photoreactive 5d-Os complex **1** a branching of the Franck-Condon excited state evolution occurs, resulting in a competition between CO-loss reactivity from the dissociative state and parallel population of an unreactive excited state.[10,32] Again, time- and temperature-dependent studies and theoretical support are needed. The CO-loss-induced photoisomerisation is characteristic for this class of dicarbonylruthenium and -osmium complexes with the lowest-energy optically accessible XLCT/MLCT excited states. Another example is the complex *trans*,*cis*-$[Ru(CO)_2(dmb)(Me)I]$ (dmb = 4,4′-tetramethyl-bpy) isomerising via the monocarbonyl transient [Ru(CO)(dmb)(Sv)(Me)I] (Sv = donor solvent) to *cis*,*cis*-$[Ru(CO)_2(dmb)(Me)I]$.[36] In this regard it is remarkable that both complex **1** and its ultimate photoproduct **2** are *trans*(Cl) isomers; although, the proposed stucture of complex **2** (see above) has not been yet confirmed by a single-crystal X-ray diffraction study.

Experimental Section

General Remarks: The supporting electrolyte Bu_4NClO_4 (TBAP; Fluka) and HPLC-grade acetonitrile (Rathburn) were used as received. Analytical-grade acetontrile and butyronitrile (purchased from Acros) were distilled from CaH_2. All syntheses and measurements were performed under dry nitrogen or argon, in a dry-box and/or using standard Schlenk techniques. For photolysis experiments, the samples were placed in a pyrex glass vessel and irradiated under argon with unfiltered light of Oriel Instruments 500-W Hg or Osram XBO 250-W Xe discharge lamps. Cyclic voltammetric measurements and bulk electrolyses were performed using a PAR Model 173 potentiostat. All cyclic voltammograms were recorded with a conventional single-compartment three-electrode cell in a

dry box (Jaram). All electrode potentials reported in this work are given relative to Ag/Ag^+ (10^{-2} M in CH_3CN containing 10^{-1} M TBAP). Conversion into the ferrocene/ferrocenium reference system can be easily done by adding −0.087 V.[37] The working electrodes for cyclic voltammetry were platinum or glassy carbon (GC) discs (active surface areas of 0.19 and 0.07 cm^2, respectively), polished carefully with a 2 μm diamond paste (Mecaprex Presi). Exhaustive electrolyses were carried out in the same cell on a platinum sheet (2 cm^2). The auxiliary electrode was a Pt wire in acetonitrile/10^{-1} M TBAP. The electrolysed solutions of complex **1** were handled in the dark to avoid photoreactions. IR and UV/Vis spectroelectrochemical experiments at variable temperatures were carried out with home-made OTTLE cells[38,39] equipped with a Pt minigrid working electrode (32 wires/cm) and CaF_2 windows. The spectroelectrochemical samples typically contained 3×10^{-3} M osmium complex and 3×10^{-1} M supporting electrolyte. The working electrode potential of the OTTLE cells was controlled with PA4 (EKOM, Czech Republic) or PAR Model 173 potentiostats. Electronic absorption spectra were recorded with Hewlett−Packard 8452 A or 8453 diode array spectrophotometers, IR spectra with Perkin−Elmer Spectrum GX FTIR or Bio-Rad FTS 7 spectrometers, and ^1H NMR spectra with a Bruker AC 250 MHz spectrometer. Mass spectra (FAB^+) were obtained with a ZAB-HF-VB analytical apparatus in a *m*-nitrobenzyl alcohol matrix. Nanosecond time-resolved absorption (TA) spectra of complex **2** were obtained by irradiating the sample with 5-ns pulses (fwhm) of a 545 nm line of a continuously tunable (360−700 nm) Coherent Infinity XPO laser. The employed experimental setup has been described previously.[40] Resonance Raman (rR) spectroscopic measurements were performed with a Dilor XY spectrometer, equipped with a Wright Instruments CCD detector. A Spectra Physics 2040E argon ion laser in combination with Coherent CR490 and CR590 dye lasers (with Coumarine 6 and Rhodamine 6G dyes) served as excitation sources under a 180° backscattering geometry. Data acquisition was controlled by Dilor Labspec 2.08 software. Wavenumbers of the resonance-enhanced Raman bands were calibrated with respect to the Raman bands of NO_3^- at 1051 and 716 cm^{-1}. Baseline deviations were corrected by using Grams software. Elemental analyses (C, H, N) were carried out in the Microanalytisches Laboratorium of Dornis & Kolbe, Mülheim a. d. Ruhr, Germany. Determination of Cl was performed argentometrically after pyrolysis according to the method of Schöniger.[41,42]

Synthesis of *trans*(Cl)-[Os(bpy)(CO)(CH_3CN)Cl_2] (2): The precursor complex *trans*(Cl)-[Os(bpy)(CO)$_2Cl_2$] (**1**) was prepared as previously described.[19] A solution of complex **1** (20 mg, 4.2×10^{-5} mol) in acetonitrile (20 mL) was illuminated with unfiltered light of a 250-W Xe lamp with continuous stirring and incidental purging with argon gas. The progress of the photoreaction was monitored by UV/Vis and IR spectroscopy. Under these conditions the complete photochemical conversion of **1** into **2** was achieved in 18 h (Figure 1). The resulting solution of **2** was concentrated to dryness, leaving behind a purple powder. Yield: ca. 18 mg (90%). ^1H NMR (250 MHz, CD_3CN, 298 K): δ = 1.96 (s, 3 H, CH_3CN), 7.40 (td, ^3J = 5.6, ^4J = 1.6 Hz, 1 H, 5′-H), 7.75 (2 td, 2 H, 4′,5-H), 8.17 (td, ^3J = 5.6, ^4J = 1.6 Hz, 1 H, 4-H), 8.33 (d, ^3J = 8.7 Hz, 1 H, 3′-H), 8.41 (d, ^3J = 8.7 Hz, 1 H, 3-H), 9.05 (d, ^3J = 5.6 Hz, 2 H, 6,6′-H) ppm. IR (CH_3CN): $\tilde{\nu}$ = 1933 [vs, ν(CO)] cm^{-1}; CsI pellet: $\tilde{\nu}$ = 1929 [vs, ν(CO)], 317 (w, ν(Os-Cl)] cm^{-1}. UV/Vis (CH_3CN): λ_{max} = 362, 534 nm. FAB-MS: *m*/*z* = 487.4 $[M + H]^+$, 446.3 $[M + H - CH_3CN]^+$, 418.3 $[M + H - CH_3CN - CO]^+$. $C_{13}H_{11}Cl_2N_3OOs$ (486.36): calcd. C 32.10, H 2.28, Cl 14.58, N 8.64; found C 31.90, H 2.19, Cl 14.81, N 8.39.

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redox series is given. Suitable examples of complexes containing Ru(CO) and $Ru(CO)_2$ moieties are $[Ru^{II}(CO)(PPh_3)(DBDiox)_2]^n$ and *cis*(CO)-$[Ru^{II}(CO)_2(DBDiox)_2]^n$, respectively; DBDiox = 3,5-di-*tert*-butyl-1,2-dioxobenzene, existing in three redox forms, as neutral *o*-quinone (Q), *o*-semiquinone (SQ) radical anion and catecholate (Cat) dianion.[26,27] The assignment of the formal oxidation states of the ruthenium(II) centre and the DBDiox ligands throughout the redox series has been supported by resonance Raman spectroscopic data.[28] Infrared CO-stretching wavenumbers for the members of the redox series $[Ru^{II}(CO)_2(DBDiox)_2]^n$ (dichloromethane, 228 K): $\tilde{\nu}$ = 2112, 2060 cm^{-1} (n = +2; DBQ/DBQ); 2091, 2037 cm^{-1} (n = +1; DBQ/DBSQ); 2056, 1998 cm^{-1} (n = 0; DBSQ/DBSQ; analogous to complex **1**); 2016, 1942 cm^{-1} (n = −1; DBSQ/DBCat); 1985, 1893 cm^{-1} (n = −2; DBCat/DBCat). Infrared CO-stretching wavenumbers for the members of the redox series $[Ru^{II}(CO)(PPh_3)(DBDiox)_2]^n$ (acetonitrile, 243 K): $\tilde{\nu}$ = 2012 cm^{-1} (n = +2; DBQ/DBQ); 1987 cm^{-1} (n = +1; DBQ/DBSQ); 1961 cm^{-1} (n = 0; DBSQ/DBSQ; analogous to complex **2**); 1909 cm^{-1} (n = −1; DBSQ/DBCat); 1861 cm^{-1} (n = −2; DBCat/DBCat).[28]

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[34] The complex [Os(bpy)$(CO)_2${C(O)O*i*Pr}Cl] is usually formed as a minor side product (yield 15−20%) during the synthesis of complex **1** conducted in 2-propanol.[19] Its purification was not attempted. A similar side reaction has also been reported for the corresponding ruthenium complexes.[35] [Os(bpy)$(CO)_2${C(O)O*i*Pr}Cl] was characterised in a mixture with complex **1**. IR (in CH_3CN): ν(CO) at $\tilde{\nu}$ = 2012, 1933 cm^{-1}. MS (FAB^+): m/z = 527 $[M + H]^+$, 491 $[M + H - Cl]^+$, 467 $[M + H - C(O)OiPr]^+$. The smaller ν(CO) wavenumbers of [Os(bpy)$(CO)_2${C(O)O*i*Pr}Cl] compared to complex **1** testify to stronger donation of electron density from the isopropoxycarbonyl ligand compared to Cl, resulting in stronger Os−CO bonds. Indeed, in contrast to complex **1**, [Os(bpy)$(CO)_2${C(O)O*i*Pr}Cl] is photostable in acetonitrile at ambient temperature and CO substitution does not occur.

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