Available online at www.sciencedirect.com

SCIENCE DIRECT®

Coordination Chemistry Reviews 249 (2005) 1327–1335

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Review

Electronic energy transfer in a dinuclear Ru/Os complex containing a photoresponsive dithienylethene derivative as bridging ligand

Ron T.F. Jukes[a], Vincenzo Adamo[b], František Hartl[a], Peter Belser[b,*], Luisa De Cola[a]

[a] *HIMS, Molecular Photonic Materials, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018WV Amsterdam, The Netherlands*
[b] *Department of Chemistry, University of Fribourg, Pérolles, 1700 Fribourg, Switzerland*

Received 16 April 2004; accepted 10 December 2004
Available online 3 March 2005

Contents

Abstract

In order to build up a multicomponent system able to perform useful light-induced functions, a dithienylethene-bridged heterodinuclear metal complex (Ru/Os) has been prepared. The compound was characterized and its photophysical properties studied in detail.

Keywords: Dinuclear metal complex; Energy transfer; Molecular device; Molecular switches; Dithienylethene; Luminescence

1. Introduction

In the last years, a great number of studies have been devoted to photochromic compounds because of their potential ability to act as photonic devices, such as data storage systems and photo-triggered switches [1]. Photoactive moieties like the dithienylethene unit are excellent examples of molecular switches, due to their reversible photochemical behavior [2]. Such units can be considered interesting candidate for the development of molecular memory and switching devices that could be integrated into more complicated circuits to lead towards the construction of molecular electronics components [3]. The simplest photoinduced processes that can result from the assembly of photoresponsive components are energy- or electron transfer reactions and eventually the electronic conductance can be measured. A step further in such a simple devices would be the control of the processes by a reversible modification of the system, upon application of an external stimulus. Amongst the most interesting input light is surely a

---

[*] Corresponding author. Tel.: +41 26 300 87 39; fax: +41 26 300 97 38.
E-mail address: peter.belser@unifr.ch (P. Belser).

doi:10.1016/j.ccr.2004.12.015

very appealing one and this is the reason why photochromic materials have attracted a lot of interest in recent years.

In a previous work [4], we prepared photochromic dithienylethene derivatives with attached homodinuclear metal units (Ru- or Os-tris(bipyridine) moieties). In the homodinuclear ruthenium complex, sensitized photocyclization from a triplet state localized on the bridging ligand was reported upon irradiation into the MLCT band of the $[Ru(bpy)_3]^{2+}$ unit. Extended photochemical and photophysical measurements on the pico- and nanosecond timescales allowed us to elucidate the mechanism of the ring-closure and opening processes in such dithienylethene switches. We have found that, in the diruthenium complex, photoinduced cyclization of the switching unit can be promoted via an efficient energy transfer from the excited metal center to the dithienylethene switch, resulting in a very high photocyclization quantum yield and nearly complete photoconversion. The corresponding diosmium complex shows an entirely different behavior. Because the osmium MLCT levels are at lower energy than the ruthenium ones, energy transfer from the excited metal center to the photochromic unit is prohibited in this complex and instead, energy transfer from the photochromic unit to the metal center now dramatically reduces the reactivity of the system.

These results have encouraged us to synthesize and study the corresponding heterodinuclear metal complex (Ru/Os) in order to examine energy transfer processes between the ruthenium and osmium centers, depending on the state of the dithienylethene switching unit (open or closed). In the present paper, the synthetic approach to the new compounds as well as their photophysical, photochemical and electrochemical properties will be given.

2. Design of new switching molecules

The study of photoinduced energy- and/or electron transfer reactions in bridged dinuclear metal complexes is an excellent possibility to gain a deep insight into the deactivation process of the excited states in such systems [5]. It allows the understanding of different factors, e.g. distance between the chromophores, geometry and electronic nature of the bridging ligand, that contribute to the assignment of the mechanism as well as to the future design of better systems. In the past, we have developed a series of dinuclear metal complexes in which the two metal centers are connected by organic, wire type bridges [6]. The communication between the two metallo-based centers can be controlled by incorporation of a photoactive switching unit [4]. The synthetic effort for the preparation of asymmetric dinuclear metal complexes (Ru/Os) is often more demanding and, therefore, a building-block technique in which prefabricated units can be used to build up the new system is recommended. The three main components of a model compound that can act as a photonic molecular device are depicted in Fig. 1.

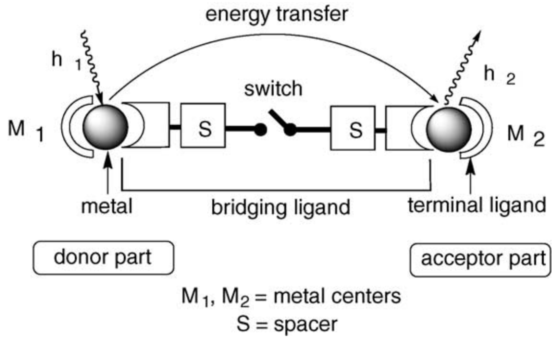


Fig. 1. Model of a dinuclear metal complex containing a switching unit.

As the donor (or sensitizer) and acceptor termini we have chosen the well known units $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$, respectively, based on their excellent photophysical and electrochemical properties [7]. Both metal complexes have good emission quantum yields and a fairly long-lived triplet excited state (about 200 ns for Ru and 40 ns for Os) and emission behavior that allow us to determine by spectroscopic techniques the occurrence of intramolecular processes. The bridging part of the dinuclear metal complex contains the dithienylethene moiety acting as a photochemical switch.

2.1. *Dithienylethene unit as switching moiety*

Among the most studied and utilized photochromic molecules are derivatives of dithienylethene containing a perfluorinated cyclopentene ring as a central part.

The photoresponsive behavior lies on the possibility of the central unit to cyclize upon irradiation in the UV region of the spectrum. The conversion to the “close” form is almost quantitative and the two forms, open and close, are thermally stable and can be converted into each other several thousands time.

Going from the open to the closed forms, the color of the system changes from colorless to blue. The ring-closure and opening processes induced by light absorption are depicted in Fig. 2.

The closing process follows the rules according to Woodward–Hoffmann, in which the photocyclization process occurs only from an antiparallel conformation of the two thienyl rings. The photochromic unit therefore exhibits all the desirable switching properties, a very high photocyclization quantum yield, high fatigue resistance, selective conversion

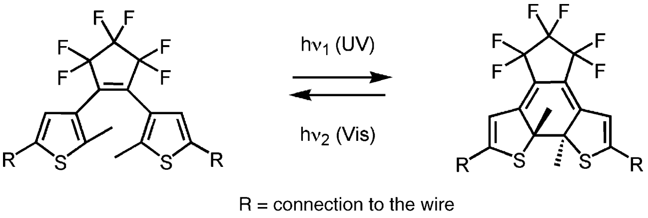
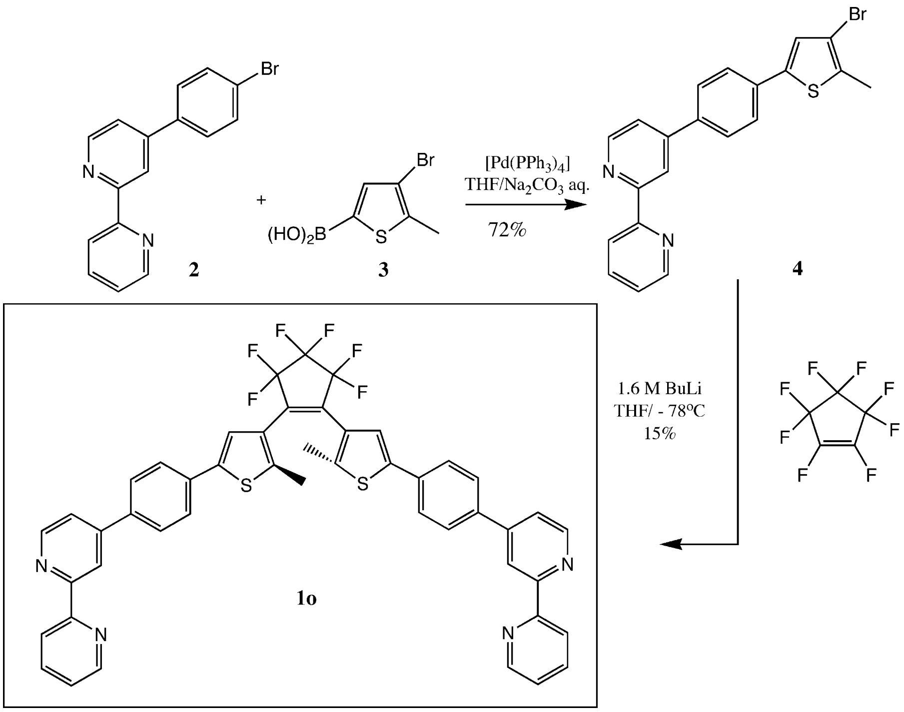
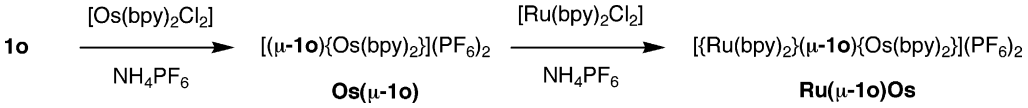


Fig. 2. Photochemical interconversion of the open and the closed form.



Scheme 1. Synthesis of the ligand **1o**.



Scheme 2. Two-step preparation of heterodinuclear complex **Ru(μ-1o)Os**.

of one form to the other, [8] and therefore could be employed as spacer in the construction of a bridging ligand.

3. Syntheses

3.1. *Preparation of switching ligand **1o** and the corresponding metal complexes **Os(1o)** and **Ru(μ-1o)Os***

The preparation of the ligand **1o** follows the protocol described in Scheme 1. 4-(4-Bromophenyl)-[2,2′]-bipyridine **2** and 3-bromo-2-methyl-5-thiopheneboronic acid **3** are coupled together by a Suzuki reaction [9] to get one of the precursor compounds **4**. A second coupling reaction between **4** and perfluorocyclopentene leads to the desired bridging ligand **1o** in moderate yield.

The metal complex formation was performed in a two-step reaction. First, nearly stoichiometric quantities of **1o** and $[Os(bpy)_2Cl_2]$ were heated in methoxyethanol at 110 °C. The mononuclear metal complex Os(1o) was isolated as PF_6^- salt and carefully purified. In a second step, the remaining coordination site of the bridging ligand was complexed with $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ under similar reaction conditions. After purification the desired dinuclear metal complex **Ru(μ-1o)Os** was isolated in overall 12% yield. The two-step reaction process is shown in Scheme 2.

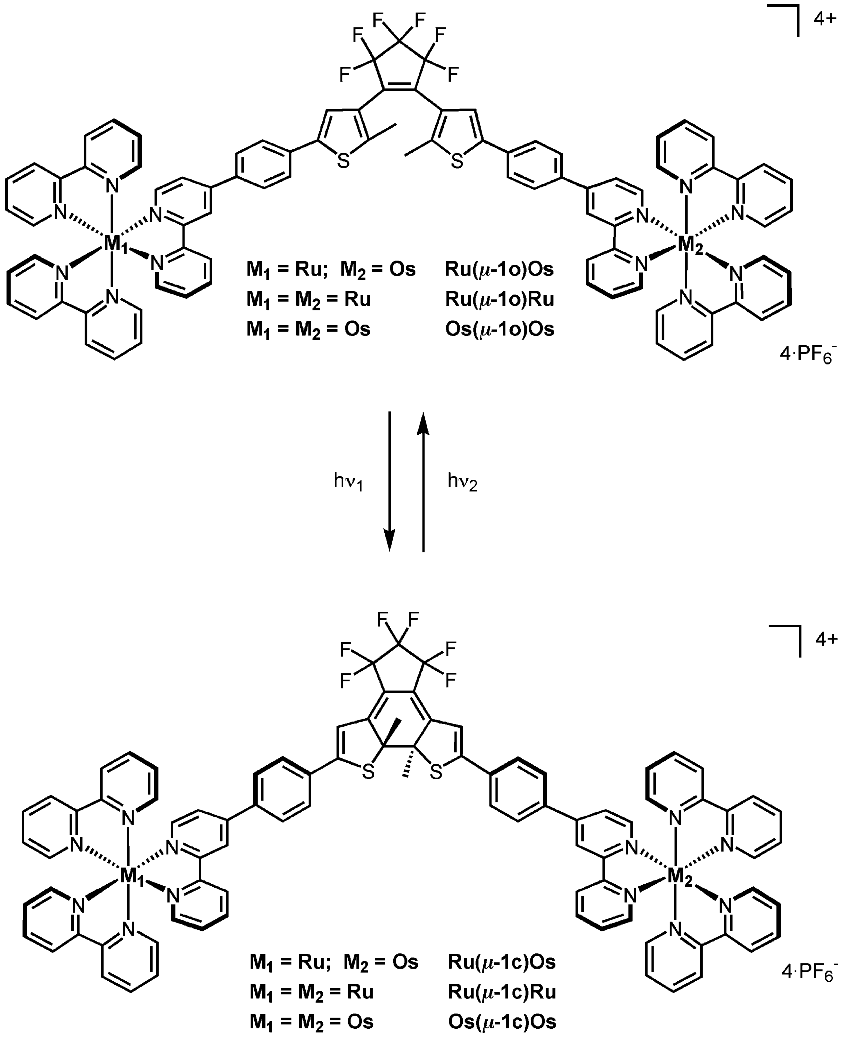
To facilitate the following discussion, all the mentioned metal complexes in their open and closed forms are depicted in Scheme 3.

4. Results and discussion

4.1. *Electronic absorption and emission properties*

The electronic absorption spectra of **Ru(μ-1o)Os** and **Ru(μ-1c)Os** in acetonitrile are shown in Fig. 3. The UV–vis absorption maxima and corresponding molar absorption coefficients are listed in Table 1. The absorption spectrum of **Ru(μ-1o)Os** is the average of the absorption spectra of complexes **Ru(μ-1o)Ru** and **Os(μ-1o)Os** [4]. This suggests that in the heterometallic complex the interactions between the Ru-based and Os-based components are weak.

A solution of open-form complex **Ru(μ-1o)Os** in acetonitrile is greenish (see Fig. 3) and turns darker green (Fig. 3) upon irradiation. The color change reflects cyclization of the



Scheme 3. Photochromism of the prepared complexes.

photochromic unit leading to a to more conjugated system, the closed-form complex **Ru(μ-1c)Os**. At the photostationary state ^{1}H NMR spectrum of a sample in CD_3OD prove that, upon irradiation with 334 nm light, 90% of the start-

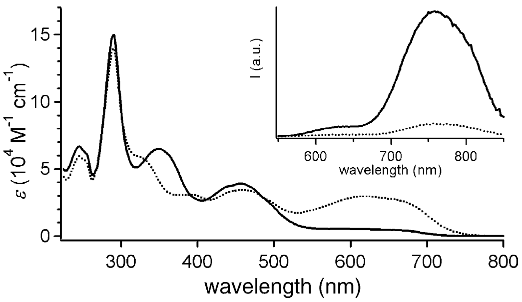


Fig. 3. UV–vis spectra of complex **Ru(μ-1o)Os** (–) and mixed **Ru(μ-1o)Os/Ru(μ-1c)Os** in the photostationary state (. . .) reached by irradiation with 334 nm light. The latter spectrum corresponds to a 90% photoconversion of **Ru(μ-1o)Os** to **Ru(μ-1c)Os**, as determined from the corresponding ^{1}H NMR spectrum. *Inset:* The corresponding decrease in emission of **Ru(μ-1o)Os** (–) caused by the conversion to the photostationary state (. . .). *Conditions:* In MeCN, at $T = 293$ K.

Table 1

UV–vis absorption maxima and absorption molar coefficients of the investigated photochromic compounds in their open and closed forms[a]

Compound	λ_{max} (nm) (ε_{max} ($\times 10^4$ M^{-1} cm^{-1}))
1o	285 (4.9), 321 (6.3)
1c	277 (4.0), 331 (4.8), 392 (sh, 1.3), 605 (2.0)
Ru(μ-1o)Ru	288 (15.6), 345 (7.1), 458 (4.2)
Ru(μ-1c)Ru	288 (14.9), 328 (sh, 6.5), 402 (3.0), 458 (3.8), 614 (3.2)
Os(μ-1o)Os	292 (15.1), 353 (6.3), 441 (3.6), 492 (3.4), 590 (0.95)
Os(μ-1c)Os	292 (13.9), 331 (sh, 5.7), 393 (3.4), 445 (3.1), 492 (3.3), 618 (3.7)
Ru(μ-1o)Os	290 (15.1), 350 (6.5), 456 (3.9), 590 (0.56)
Ru(μ-1c)Os	290 (13.8), 329 (sh, 5.8), 396 (3.1), 457 (3.4), 617 (3.3)

[a] In MeCN, at $T = 293$ K.

Table 2
Emission maxima (λ_{max}), lifetimes (τ) and quantum yields (φ_{em}) of investigated photochromic complexes **Ru(μ-1o)Ru**, **Os(μ-1o)Os** and **Ru(μ-1o)Os**[a]

Compound	λ_{max} (nm)		τ (ns)				φ_{em}[b]			
	Ru	Os	Ru		Os		Ru		Os	
			Aerated	Deaerated	Aerated	Deaerated	Aerated	Deaerated	Aerated	Deaerated
Ru(μ-1o)Ru	630		140	310			0.006 (334) 0.007 (450)	0.014 (334) 0.014 (450)		
Os(μ-1o)Os		757			44	62			0.004 (334) 0.004 (450)	0.005 (334) 0.006 (450)
Ru(μ-1o)Os	630[c]	758	0.07 0.61		0.56[d] 46		2×10^{-4} (471)		0.0035 (471)	

[a] In MeCN, at $T = 293$ K, all values obtained from single measurements.
[b] Excitation wavelength (nm) in brackets.
[c] The ruthenium emission appears as a shoulder of the osmium emission band and the reported emission maximum could merely be estimated.
[d] Growth of the emission.

ing **Ru(μ-1o)Os** complex is converted to the closed form, **Ru(μ-1c)Os**.

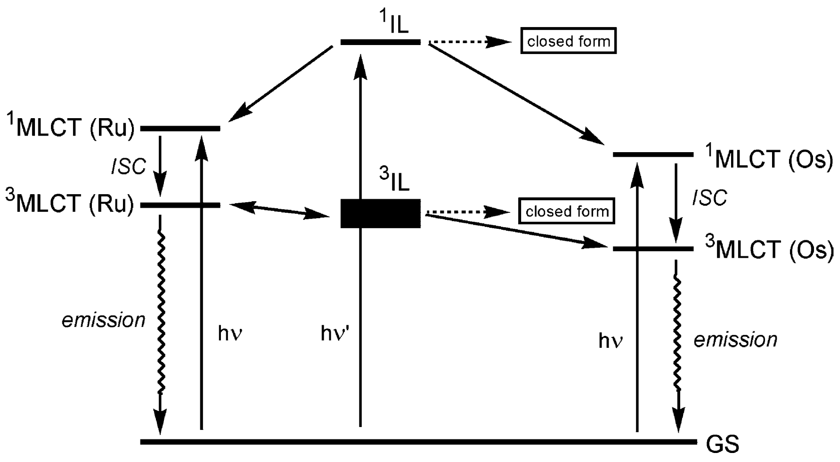
Besides the spectral changes occurring in the UV–vis absorption spectrum, dramatic changes are observed in the emission behavior.

The emission spectrum of **Ru(μ-1o)Os** in aerated acetonitrile (Fig. 3, inset) was recorded upon excitation with 471 nm light, which corresponds to the isoabsorptive wavelength for the Ru-bpy and Os-bpy MLCT bands. It shows both ruthenium-based and osmium-based emissions, centered at about 630 and 730 nm, respectively. From a comparison of the emission intensities we can conclude that the ruthenium moiety emits much less than in the homodinuclear complex, while the osmium emission intensity is about 90% of that of **Os(μ-1o)Os** (Table 2). This result reveals that the energy transfer from the ruthenium to osmium centers in **Ru(μ-1o)Os** is very efficient and the quenching of the ruthenium moiety (see also the excited state lifetime in the next section) is in large part due to the energy transfer and in much minor contribution to the photoreaction.

The excited state lifetimes mirror the emission spectra discussed above for the osmium-based component. In fact the osmium excited state lives 46 ns (Table 2), which is essentially identical to the emission lifetime of **Os(μ-1o)Os** (44 ns) [4]. The lifetime of the ruthenium emission is strongly reduced compared to **Ru(μ-1o)Ru**. The emission decay is bi-exponential, with components of 0.07 and 0.61 ns. We believe that the longest component is due to the quenched ruthenium unit in the open form and the shortest one is due to a small amount of the ruthenium closed form that is obtained during the measurement upon excitation in the UV region. The energy transfer process can also be monitored by the rise time of 0.56 ns observed in the osmium decay measurements. This value agrees well with the long decay component (0.61 ns) of the ruthenium emission.

4.2. Photocyclization

The cyclization reaction of **Ru(μ-1o)Os** is insensitive to oxygen, but it is wavelength-dependent. Upon irradiation into the IL (intraligand) band at 334 nm, the cyclization occurs with a quantum yield approximately twice as high as upon irradiation into the MLCT (metal-to-ligand charge transfer) band at 450 nm (Table 3). Taking into account the energy schemes proposed in our previous article [4], this difference can easily be explained (Scheme 4).



Scheme 4. Qualitative energetic scheme for complex **Ru(μ-1o)Os**.

Table 3
Quantum yields φ_λ[a] for the photocyclization of dithienylethene **1o** and homodinuclear complexes **Ru(μ-1o)Ru** and **Os(μ-1o)Os**

Compound	φ_{334}		φ_{450}	
	Aerated	Deaerated	Aerated	Deaerated
1o	0.72	0.74	[b]	[b]
Ru(μ-1o)Ru	0.37	0.88	0.38	0.80
Os(μ-1o)Os	0.0045	0.0041	[c]	[c]
Ru(μ-1o)Os	0.010	0.010	0.0042	0.0045

[a] In MeCN, at $T = 293$ K, all values obtained from single measurements; $\lambda_{exc} = 334$ or 450 nm.
[b] Compound **1o** does not absorb at 450 nm.
[c] No photoreaction.

Excitation with 334 nm light initially populates the ^{1}IL state, localized on the bridging ligand. From this state, energy is transferred efficiently to the MLCT states on either ruthenium or osmium, but as already found for **Os(μ-1o)Os** [4], the fast ^{1}IL-state cyclization reaction can compete with this energy transfer process. As shown for **Ru(μ-1o)Ru**, [4] an equilibrium exists between the ruthenium ^{3}MLCT and the reactive ^{3}IL state on the photochromic unit. Even though an efficient energy transfer to the osmium ^{3}MLCT state consequently depopulates both states, this process is sufficiently slow to allow some cyclization to occur from the ^{3}IL state. Upon irradiation with 450 nm light, only the two ^{1}MCLT states are populated. Therefore, cyclization cannot take place from the ^{1}IL state, but only from the ^{3}IL state. Indeed, the difference of 5.6×10^{-3} between the two photocyclization quantum yields φ_{334} and φ_{450} (Table 3) corresponds reasonably well to $\varphi_{334} = 4.3 \times 10^{-3}$ for **Os(μ-1o)Os**, which is supposed to be exclusively due to cyclization from the ^{1}IL state.

4.3. Transient absorption spectra of **Ru(μ-1o)Os**

Fig. 4 presents the nanosecond transient absorption spectra of **Ru(μ-1o)Os** excited at 450 nm (up to 90 ns). The spectral changes observed upon irradiation at 334 nm are qualitatively very similar. The spectra show the MLCT bleach around 460 nm. From the decay of the transient species, the lifetime of the observed excited state has been determined to be 44 ns. This is in excellent agreement with the excited state lifetime of 46 ns that was obtained from the decay of the osmium emission of **Ru(μ-1o)Os** (Table 2). These observations, and the fact that the transient absorption spectrum exhibits the same features as that obtained for **Os(μ-1o)Os** under the same conditions [4], point to a ^{3}MLCT state localized on the Os(bpy)$_3$-part of the system. After the decay of the excited state species, an absorption remains that can be ascribed to the formation of photoproduct **Ru(μ-1c)Os**. The steady state difference spectrum between **Ru(μ-1o)Os** and **Ru(μ-1c)Os** is shown in Fig. 4 as reference. Going from 334 nm excitation to 450 nm excitation, the absorptions of the photoproduct **Ru(μ-1c)Os** at 90 ns differ by about the same factor as the corresponding cyclization quantum yields φ_{334} and φ_{450} (Table 3).

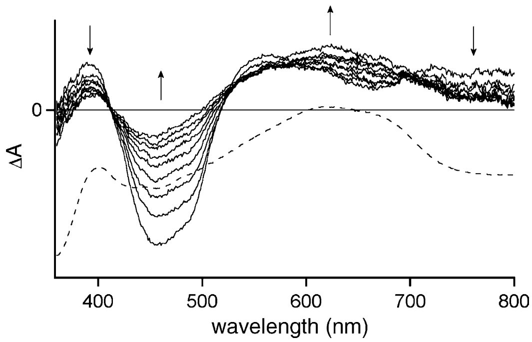


Fig. 4. Transient absorption difference spectrum of **Ru(μ-1o)Os**, with 10 ns intervals between frames. The dotted line represents the shape of the steady state difference spectrum between **Ru(μ-1c)Os** and **Ru(μ-1o)Os**. *Conditions:* In MeCN, in air-equilibrated solution, at $T = 293$ K, $\lambda_{exc} = 450$ nm.

From the nanosecond transient absorption spectra it is not directly apparent whether the photoproduct is formed prior to the decay of the osmium ^{3}MLCT state or on the same timescale, which would indicate equilibrium between this and the reactive states. If the latter explanation were correct, however, oxygen dependence could be observed for the cyclization quantum yield. Also, no cyclization was observed for **Os(μ-1o)Os** upon irradiation into the MLCT band, proving that the energy difference between the ^{3}IL and osmium ^{3}MLCT states is too large for an equilibrium to exist. Furthermore, if a sample of **Ru(μ-1o)Os** is excited at 625 nm (i.e., directly into the osmium ^{3}MLCT state), the same transient is observed, but it decays completely to the ground state and no formation of the cyclized photoproduct is observed. Therefore, it can be safely concluded that upon excitation at 334 or 450 nm the cyclized product is formed within the laser pulse, and all subsequent changes in the transient absorption spectra can be attributed to the decay of the ^{3}MLCT$_{Os}$ state.

Therefore, transient absorption spectra were recorded in the femto–picosecond range. In the spectra of **Ru(μ-1o)Os** excited with 450 nm light, changes are observed within the first few picoseconds. A formation of a band at about 500 nm is observed within few hundred picoseconds. We believe that such absorption is due to the formation of the ^{3}IL state which than reacts to give the photoproduct (**Ru(μ-1c)Os**). After this initial period, no further changes take place and the resulting spectrum is essentially the same as that obtained for the first frame of the nanosecond experiment. No obvious changes in the shape or intensity of the bleached MLCT band, expected for a ruthenium-to-osmium ^{3}MLCT energy transfer, are observed. From this observation we conclude that the equilibrium between the ^{3}MLCT and ^{3}IL states is established within a few picoseconds. Thus, the observed picosecond transient absorption spectrum is a combination of the spectra corresponding to the osmium ^{3}MLCT and dithienylethene ^{3}IL states. From the measurements on **Ru(μ-1o)Ru** we know that the latter spectrum is broad and essentially featureless, which explains why no clear changes can be observed in the transient absorption spectra as a result of the energy transfer to the osmium ^{3}MLCT state.

Upon excitation of **Ru(μ-1o)Os** at 450 nm, approximately 50% of the energy will be absorbed by the ruthenium moiety, and 50% by the osmium unit since their MLCT states overlaps and have very similar extinction molar coefficient. The photocyclization quantum yield of **Ru(μ-1o)Os** is ca. 180 times lower than that of **Ru(μ-1o)Ru**. Considering that only 50% of the absorbed light results in the population of the ruthenium MLCT and, subsequently, the reactive ^{3}IL state, the photocyclization efficiency is reduced 90 times. Such pronounced reduction implies that energy transfer to the osmium ^{3}MLCT state is competing with the photocyclization. The emission measurements yielded a time constant of 0.56 ns for the energy transfer process. This process must be then much slower than the equilibration between the ruthenium ^{3}MLCT and the ^{3}IL states. Therefore, the time constant of 0.56 ns can be considered as a total rate for the energy transfer from the ^{3}MLCT$_{\mathrm{Ru}}$ and ^{3}IL states to the ^{3}MLCT$_{\mathrm{Os}}$ state. The rate constant k_{ET} for this process is thus approximately $1.8 \times 10^9\ \mathrm{s}^{-1}$.

4.4. Transient absorption spectra of *Ru(μ-1c)Os*

Light excitation of **Ru(μ-1c)Os** at 450 nm gives a nanosecond transient absorption spectrum that is essentially identical to those observed for **Ru(μ-1c)Ru** and **Os(μ-1c)Os** under these conditions [4]. By analogy, the spectrum can be assigned to a ^{3}IL state of the photochromic unit. After the decay of the excited-state species an absorption remains, clearly showing that, in this case, open complex **Ru(μ-1o)Os** is formed. This photocycloreversion could occur either from the singlet or the triplet excited state of the dithienylethene moiety. Unfortunately, our data do not allow distinguishing between these two possibilities.

On the picosecond timescale, a bleach can initially be observed at 475 nm, due to the population of the ruthenium and osmium MLCT states. This feature disappears quickly. At the same time, a band grows at ca. 540 nm, accompanied by a bleach at 660 nm (see Fig. 5). The resulting spectrum is that observed on the nanosecond timescale and is attributed to the ^{3}IL state. Since the energy transfer from the ^{3}MLCT to the ^{3}IL state is essentially the fastest process in the system, we assign the calculated time constant of 4 ps to this process, which corresponds to a rate constant $k_{\mathrm{ET}} = 2.5 \times 10^{11}\ \mathrm{s}^{-1}$. These values nicely compare with the time constant of 5 ps ($k_{\mathrm{ET}} = 2 \times 10^{11}\ \mathrm{s}^{-1}$) determined in a separate experiment for **Ru(μ-1c)Ru**. It can be concluded that the energy scheme for **Ru(μ-1c)Ru** [4] also applies to **Ru(μ-1c)Os**.

4.5. Electrochemistry

Cyclic and Osteryoung square wave voltammetric measurements were performed on **Os(μ-1o)Os** and **Ru(μ-1o)Os**. The corresponding redox potentials against Fc/Fc$^+$ are listed in Table 4. For **Ru(μ-1o)Os**, two distinct oxidation waves rise at $E_{1/2} = +0.44$ V and +0.86 V. These anodic potentials are virtually the same as those found for **Os(μ-1o)Os** and **Ru(μ-1o)Ru** [4] and for $[\mathrm{Os(bpy)_3}]^{2+}$ [10] and $[\mathrm{Ru(bpy)_3}]^{2+}$ [11], and can thus be assigned to the oxidations of the osmium(II) and ruthenium(II) center, respectively. The fact that the oxidation potentials are nearly the same for **Os(μ-1o)Os** and **Ru(μ-1o)Ru**, and $[\mathrm{Os(bpy)_3}]^{2+}$ and $[\mathrm{Ru(bpy)_3}]^{2+}$, respectively, indicates that the electronic properties of the metal centers are not significantly affected by the presence of the bridging ligand. Also, the cathodic steps are not affected by the replacement of a ruthenium center by an osmium, the reduction potentials and sequence in the case of **Ru(μ-1o)Os** are the same as reported for **Ru(μ-1o)Ru** [4].

Table 4
Electrochemical data for selected compounds under study[a] and two reference compounds

Compound	T (K)	$E_{1/2}$ (V)					$E_{\mathrm{p,c}}$ (V)[b]
		Ru$^{\mathrm{II/III}}$	Os$^{\mathrm{II/III}}$	$(\mathrm{bpy}^{0/-})_{\mathrm{I}}$	$(\mathrm{bpy}^{0/-})_{\mathrm{II}}$	$(\mathrm{bpy}^{0/-})_{\mathrm{III}}$	
$[\mathrm{Ru(bpy)_3}]^{2+}$[c]	293	+0.89		−1.72	−1.93	−2.18	
$[\mathrm{Os(bpy)_3}]^{2+}$[d]			+0.40	−1.60			
1o	293						−2.12[e]
Ru(μ-1o)Ru	293	+0.86		−1.73	−1.90	−2.17	−1.86
	208	+0.84		−1.71	−1.90	−2.13	−2.04
Os(μ-1o)Os	293		+0.44				
Ru(μ-1o)Os	293	+0.86	+0.43	−1.70	−1.90	−2.19	−1.85
1c	293						−1.37[f]
Ru(μ-1c)Ru	293						−1.27[f]

[a] Redox potentials (V vs. Fc/Fc$^+$) have been determined from combined cyclic and Osteryoung square-wave voltammetric scans. *Conditions:* MeCN (unless stated otherwise), Pt disc working microelectrode, $v = 100\ \mathrm{mV\,s^{-1}}$ (cyclic voltammetry), $f = 30$ Hz (s–w voltammetry).

[b] Irreversible reduction localized on the photochromic dithienylethene unit.

[c] Ref. [11].

[d] Ref. [10], potentials were reported vs. SCE. Potentials vs. Fc/Fc$^+$ reported here were calculated from these values, assuming a value of +0.31 for Fc/Fc$^+$ vs. SCE.

[e] Successive reversible reduction of a secondary reduction product found at −2.47 V for **1o**.

[f] Successive irreversible reduction of a secondary reduction product found at $E_{\mathrm{p,c}} = -1.82$ V for **1c** and $E_{\mathrm{p,c}} = -1.37$ V for **Ru(μ-1c)Ru**.

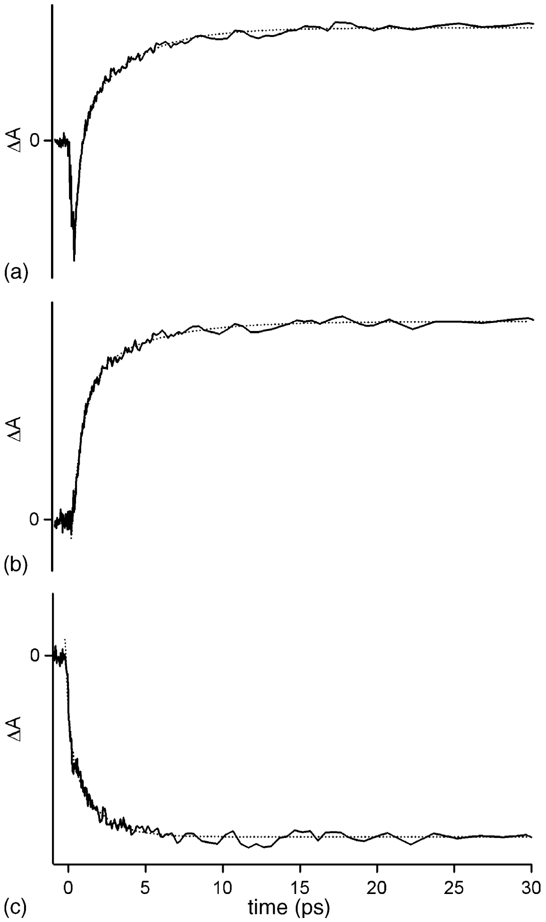


Fig. 5. Transient absorption kinetics measured for **Ru(μ-1c)Os** at (a) 475 nm, (b) 540 nm, (c) 660 nm. *Conditions:* In MeCN, in air-equilibrated solution, at $T = 293$ K, $\lambda_{exc} = 450$ nm.

5. Conclusions

A new heteronuclear, bridged metal complex (Ru/Os) containing a dithienylethene photo-switching unit is described. The synthetic protocol as well as a detailed discussion of the photophysical properties and photochemistry are presented. The bridging unit in the dinuclear metal complex **Ru(μ-1o)Os** (open form) allows an efficient energy transfer from the excited ruthenium to the osmium center. When the switching unit is present in its closed form, the energy level of the dithineylethene unit is below the energy levels of the two metal centers quenching both emissions. The closed switching unit then acts as a trap for the excited states of both coordinated metal termini.

6. Experimental section

Ligand **1o**, complexes **[{Ru(bpy)$_2$}$_2$(μ-1o)](PF$_6$)$_4$ (Ru(μ-1o)Ru)** and **[{Os(bpy)$_2$}$_2$(μ-1o)](PF$_6$)$_4$ (Os(μ-1o)Os)** were synthesized as described in literature [4].

General techniques: The same experimental techniques and methods were used as mentioned in the literature [4].

[{Os(bpy)$_2$}(μ-1o)](PF$_6$)$_2$, Os(1o). A solution of **1o** (51 mg, 0.062 mmol) and [Os(bpy)$_2$Cl$_2$] (34 mg, 0.059 mmol) in methoxyethanol (20 mL) was heated progressively until 110 °C under an argon atmosphere. The reaction was monitored by TLC, $R_f = 0.2$ (mononuclear), $R_f = 0.6$ (dinuclear). After 8 h, the solvent was distilled off under vacuum and the residue was treated with an aqueous solution of 10% NH$_4$PF$_6$. The precipitate was collected by filtration and washed with water. The crude product was purified by plate chromatography (SiO$_2$) using a mixture of acetonitrile/methanol/water/saturated solution of potassium nitrate (40:10:10:1) as eluent. The main band was scratched out and the product was isolated with a 1% NH$_4$PF$_6$/acetone solution as eluent. After adding water, the organic solvent was removed, and a green solid (20 mg, 21%) was recovered by filtration. ^{1}H NMR (300 MHz, CD$_3$OD): δ 2.08 (d, 6H), 7.40 (m, 5H), 7.50 (m, 3H), 7.77 (m, 12H), 7.95 (m, 10H), 8.37 (d, 1H), 8.63 (s, 1H), 8.69 (m, 6H), 8.88 (d, 1H), 8.96 (s, 1H). ^{13}C NMR (400 MHz, CD$_3$OD): δ 14.7, 122.6, 122.7, 122.9, 124.4, 124.9, 125.5, 125.8, 126.1, 126.3, 127.3, 128.9, 129.3, 129.4, 135.6, 135.9, 136.7, 138.6, 138.9, 142.5, 143.1, 144.1, 149.6, 150.2, 150.3, 151.0, 151.7, 151.8, 157.1, 157.8, 160.5, 160.5. MS (ESI), *m/z*: $[M - \text{PF}_6]^{1+} = 1477.26$, $[M - 2\text{PF}_6]^{2+} = 666.15$. HRMS (ESI), *m/z*: $[M - 2\text{PF}_6]^{2+}$ calcd. for C$_{67}$H$_{46}$F$_7$N$_8$Os(192)S$_2$: 666.1393; found: 666.1397.

[{Ru(bpy)$_2$}(μ-1o){Os(bpy)$_2$}](PF$_6$)$_4$, Ru(μ-1o)Os. A solution of **Os(μ-1o)** (20 mg, 0.012 mmol) and Ru(bpy)$_2$Cl$_2$·2H$_2$O (7 mg, 0.013 mmol) in methoxyethanol (10 mL) was refluxed during 15 h under an argon atmosphere. The solvent was distilled off under vacuum and the residue was treated with an aqueous solution of 10% NH$_4$PF$_6$. The precipitate was collected by filtration and washed with water. The crude product was purified by plate chromatography (SiO$_2$) using a mixture of acetonitrile/methanol/water/saturated solution of potassium nitrate (40:10:10:1) as eluent. The main green brown band was scratched out from the plate and the compound was isolated with a 1% NH$_4$PF$_6$/acetone solution as eluent. After adding water, the organic solvent was removed, and a dark powder (16 mg, 56%) was recovered by filtration. ^{1}H NMR (400 MHz, CD$_3$OD): δ 2.09 (s, 6H), 7.49 (m, 12H), 7.82 (m, 14H), 7.99 (m, 12H), 8.16 (m, 6H), 8.72 (m, 8H), 8.91 (d, 2H, $^3J = 9.0$), 8.98 (d, 2H, $^3J = 9.0$). ^{13}C NMR (400 MHz, CDCl$_3$): δ 13.6, 121.6, 121.7, 123.9, 124.6, 124.8, 125.1, 125.3, 126.3, 127.9, 128.0, 128.3, 128.4, 135.0, 135.6, 137.6, 138.2, 141.6, 143.0, 148.6, 149.3, 150.2, 150.7, 150.8, 151.6, 157.5, 157.7, 157.9, 159.4, 159.9. MS (ESI), *m/z*: $[M - \text{PF}_6]^{1+} = 1079.07$, $[M - 2\text{PF}_6]^{2+} = 467.07$. HRMS (ESI), *m/z*: $[M - 4\text{PF}_6]^{4+}$ calcd. for C$_{87}$H$_{62}$F$_6$N$_{12}$Os(192)Ru(102)S$_2$: 436.5805; found 436.5800.

Acknowledgements

We thank the National Swiss Science Foundation for funding through the NFP 47 program. We also thank the EC (contract G5RD-CT-2002-00776, MWFM) for financial support.

References

[1] (a) Special issue on molecular materials in electronic and optoelectronic devices, Acc. Chem. Res. 32 (1999);
(b) H. Dürr, E. Bouas-Laurent (Eds.), Photochromism. Molecules and Systems, Elsevier, Amsterdam, 1990;
(c) V. Balzani, A. Credi, F.M. Raymo, J.F. Stoddart, Angew. Chem. Int. Ed. 39 (2000) 3348;
(d) R.E. Martin, F. Diederich, Angew. Chem. Int. Ed. 38 (1999) 1351.

[2] (a) J.C. Crano, R.J. Guglielmetti, Organic Photochromic and Thermochromic Compounds, vol. 1, Kluwer, Dordrecht, 1999;
(b) B.L. Feringa, Molecular Switches, Wiley-VCH, Weinheim, 2001.

[3] (a) M. Irie (Ed.), Special issue on photochromism: memories and switches, Chem. Rev. 100 (2000);
(b) C. Joachim, J.K. Gimzewsky, A. Aviram, Nature 408 (2000) 541;
(c) F.M. Raymo, Adv. Mater. 14 (2002) 401;
(d) V. Balzani, A. Credi, M. Venturi, Chem. Phys. Chem. 4 (2003) 49.

[4] R.T.F. Jukes, V. Adamo, F. Hartl, P. Belser, L. De Cola, Inorg. Chem. 43 (2004) 2779.

[5] (a) V. Adamo, P. Belser, Chimia 57 (2003) 169;
(b) L. De Cola, P. Belser, Coord. Chem. Rev. 177 (1998) 301;
(c) A. Harriman, R. Ziessel, Coord. Chem. Rev. 171 (1998) 331;
(d) L. De Cola, P. Belser, V. Balzani (Eds.), Molecular-Level Electronics, Imaging and Information, Energy and the Environment, Section 1: Molecular-Level Electronics, vol. 5, Wiley-VCH, Weinheim, Germany, 2000 (chapter 3).

[6] (a) L. De Cola, V. Balzani, F. Barigelletti, L. Flamigni, P. Belser, A. von Zelewsky, M. Frank, F. Vögtle, Inorg. Chem. 32 (1993) 5228;
(b) L. De Cola, V. Balzani, F. Barigelletti, L. Flamigni, P. Belser, S. Bernhard, Recl. Trav. Chim. Pays-Bas 114 (1995) 534;
(c) V. Balzani, F. Bargelletti, P. Belser, S. Bernhard, L. De Cola, L. Flamigni, J. Phys. Chem. 100 (1996) 16786;
(d) P. Belser, S. Bernhard, Synthesis (1996) 192;
(e) M. Frank, M. Nieger, F. Vögtle, P. Belser, A. von Zelewsky, L. De Cola, V. Balzani, F. Barigelletti, L. Flamigni, Inorg. Chim. Acta 242 (1996) 281;
(f) P. Belser, S. Bernhard, Ch. Blum, A. Beyeler, L. De Cola, V. Balzani, Coord. Chem. Rev. 190–192 (1999) 155;
(g) B. Schlicke, P. Belser, L. De Cola, E. Sabbioni, V. Balzani, J. Am. Chem. Soc. (1999) 4207;
(h) G. Albano, P. Belser, L. De Cola, M.-T. Gandolfi, J. Chem. Soc., Chem. Commun. (1999) 1171.

[7] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, Coord. Chem. Rev. 84 (1988) 85.

[8] M. Irie, Chem. Rev. 100 (2000) 1685.

[9] (a) N. Miyaura, A. Suzuki, Org. Synth. 68 (1990) 130;
(b) T. Ishiyama, N. Miyaura, A. Suzuki, Org. Synth. 71 (1993) 89.

[10] E.M. Kober, B.P. Sullivan, W.J. Dressick, J.V. Caspar, T.J. Meyer, J. Am. Chem. Soc. 102 (1980) 7383.

[11] (a) N.E. Tokel-Takvoryan, R.E. Hemingway, A. Bard, J. Am. Chem. Soc. 95 (1973) 6582;
(b) N. Sutin, C. Creutz, Adv. Chem. Ser. 168 (1978) 1.