Synthesis and Properties of Dinuclear Complexes with a Photochromic Bridge: An Intervalence Electron Transfer Switching "On" and "Off"

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Two cyclometallated Ru(bpy)$_2$(pp) units (bpy = 2,2′-bipyridine; pp = 2-phenylpyridine) were grafted via ethynyl spacers onto the photochromic cores of the norbornadiene or dithienylethene families, to give the bimetallic ruthenium(II) complexes **1** and **2a**, respectively. Two aspects of these compounds were studied: (i) photoisomerization (norbornadiene to quadricyclane for **1**, open form to closed form of the dithienylethene core for **2a**), and (ii) intervalence transitions in the mixed-valence ruthenium(II–III) state, with determination of the metal–metal electronic coupling (V_{ab}) by Hush's equation. Moderate metal–metal electronic coupling (0.068 eV) was found for **1**, but **1** cannot be isomerized into the quadricyclane form. On the other hand, **2a** can be reversibly photoisomerized to the closed form **2b**. An iodine(III) reagent, the triflate salt of bis(pyridyl)phenyliodonium, was used for the oxidation of **2a** and **2b**. During these oxidations, an intervalence band due to intramolecular electron transfer between ruthenium(II) and ruthenium(III) was detected for **2b**, but not for **2a**. This switching "on" or "off" of the intervalence transition is rationalized with extended Hückel calculations. Finally, the molecular orbital calculation explains the observed tendency of the closed form **2b** to reopen upon oxidation.

Introduction

Switching at the molecular scale is one of the great challenges of molecular electronics.[1a] It is important to devise molecules able to reproduce one of the most important functions of electronic devices, that is, the ability to change in a controlled manner between a "conducting" and a "nonconducting" state, which is a prerequisite for the realization of logical functions. Ideally, such molecules should be used in nanometric-scale devices involving a unique molecule, and experiments along these lines are in progress.[1b–1d] However, due to the difficulty of experiments dealing with unique molecules, one has to rely, for some time still, on more conventional studies involving a (noninteracting) ensemble of molecules in solution, probed by spectroscopic methods. An important issue is the ability to transfer electrons intramolecularly between clearly identified sites.

Intramolecular electronic coupling between two redox sites can be probed by the intervalence transition occurring in the near-infrared for the mixed-valence state.[2] Hush's equation[3] allows the intensity of this transition to be used to estimate the electronic coupling term V_{ab}, that is, the efficiency of the bridge at mediating electron transfer between the distant redox sites.

In the search for molecules able to show a switching effect, we have tried to introduce as bridging ligand a photochromic moiety exhibiting two states ("on" and "off") with respect to electronic coupling. Symmetrical photochromic cores were selected to preserve the formal "exchangeability" of the two metallic centers. The association of photochromism and intervalence electron transfer is schematically represented in Figure 1a.

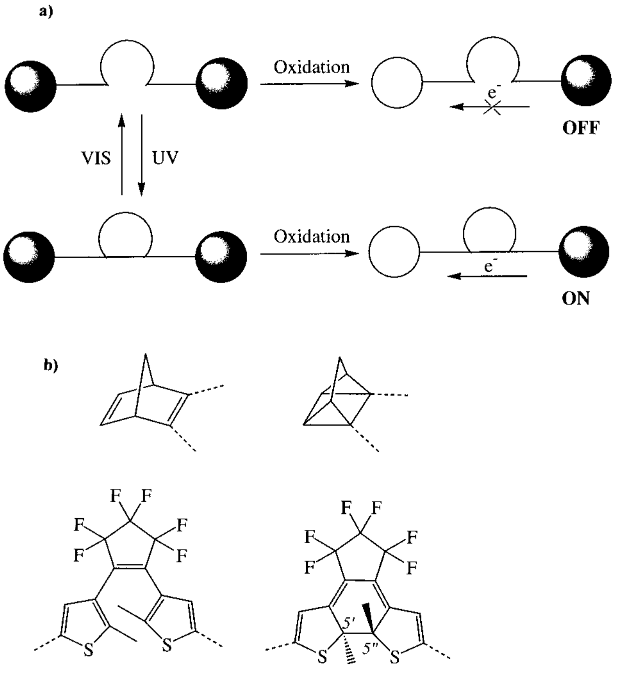

Figure 1. (a) Principle of the association of a switching moiety with intervalence electron transfer; (b) photochromic processes considered in the present paper; in the case of dithienylethene derivatives, the nomenclature **Na** and **Nb** will be used for the open and closed forms, respectively

A previous attempt used the norbornadiene/quadricyclane isomerization in a bis(pentaammineruthenium) complex of dicyanonorbornadiene.[4] Extinction of the intervalence band occurred in the dicyanoquadricyclane complex, but the photoreaction was not reversible and the

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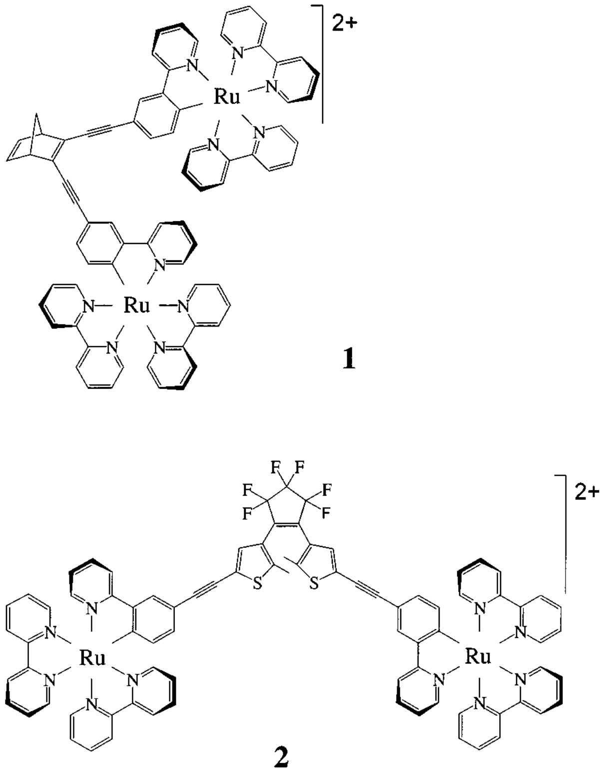
ruthenium−nitrile bond was not stable enough for further studies.

In other respects, as photochromic moieties, systems of the dithienylethene family, discovered by Irie et al,[5] exhibit several attractive characteristics: good stability, reversibility, high quantum yield, separated absorption spectra for the two forms, resistance to fatigue after multiple cycling. Their interest (particularly when the central double bond is locked by a perfluorocyclopentene cycle), was recognized by Lehn et al.[6] who described several associations of such photochromic parts with redox groups and their peculiar electrochemical and nonlinear optical properties. Thus, complex functions were obtained, involving the association of photochromism and electrochromism, that is, the sensitivity to two different stimuli.[6]



1

2

Scheme 1. Target molecules; **2** is represented as the open form **2a**

The redox sites we report on here are cyclometalated ruthenium complexes (Scheme 1). Cyclometalation has been shown to confer stability on the complexes, and, furthermore, strong electronic coupling, resulting in intense intervalence transitions, occurs.[2a,7,8] Strictly speaking, the coupling depends also on the nature of the spacer, but it turns out that most cyclometalated compounds associated with spacers such as phenylene units, or combinations of ethynyl units and aromatic groups are efficient for electron transfer. In the present paper, we report on our use of analogues of $[Ru(bpy)_3]^{2+}$, where one 2,2′-bipyridine is formally replaced by a deprotonated 2-phenylpyridine ligand.[9] We have recently shown how this easily functionalized cyclometalated complex could be used as an organometallic synthon.[9,10] Gram quantities are easily prepared and the corresponding chemistry has proved to be flexible and versatile. It is, in particular, possible to introduce ethynyl residues, which are efficient conjugated spacers, for example in tolane derivatives.[11] Such a "building block" approach involving a palladium-catalyzed cross-coupling reaction constitutes a very convergent synthesis of conjugated dinuclear complexes.

The present paper describes the properties of binuclear complexes with cyclometalated units as terminal groups, and with photochromic bridges such as norbornadiene or dithienylethene (Figure 1b). Their photochemistry in the homovalent $Ru^{II}-Ru^{II}$ state was studied. Note that the transformations expected are opposite: in the case of norbornadiene, photoisomerization drives the system from a conjugated state ("on") to a nonconjugated one ("off"), while the reverse is true when cyclization of the dithienylethene moiety occurs.

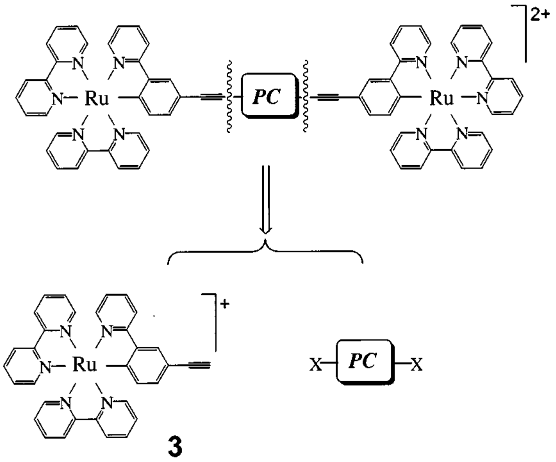
Results and Discussion

Syntheses

The general retrosynthetic route we adopted relies on extensive use of a palladium-catalyzed ethynylation reaction, which involves cross-coupling between a substituted acetylene and an electrophilic sp^2-hybridized carbon atom.[12] The disconnection we selected, outlined in Scheme 2, is mostly based on the fact that a ruthenium complex bearing a protected ethynyl group was readily available. While keeping the synthesis highly convergent, this also enabled us to circumvent some reactivity problems due to the use of the brominated ruthenium complex precursor.[10]

Organometallic Synthon

Two complexes, with an acetylene group protected by a trimethylsilyl (TMS) or by a 2-hydroxypropan-2-yl (POH) group, were available.[9] However, fluoride-induced desilylation of the TMS-protected compound was always accompanied by extensive decomposition of the cyclometalated part. On the other hand, the easily purified POH-protected alkyne **4** was found to be quantitatively deprotected with

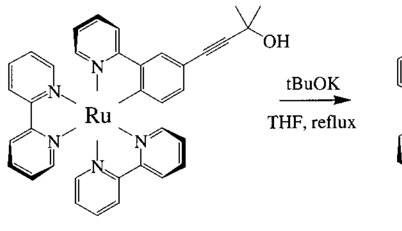


3

Scheme 2. General retrosynthetic route (PC = photochromic unit) *t*BuOK in refluxing THF. No purification was found to be necessary, apart from removal of potassium salts and anion metathesis, thereby unnecessary exposure to air could be avoided (Scheme 3).

Photochromic Synthons

To use low reaction temperatures for the final cross coupling, we focused our attention on iodinated precursors of the photochromic core.



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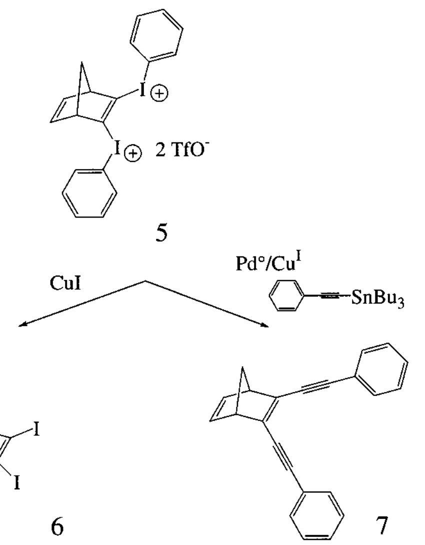
Scheme 3. Organometallic synthon



5

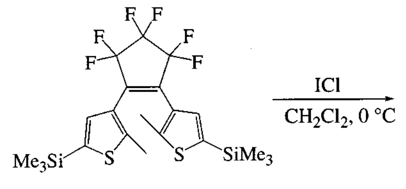
6 7

Scheme 4. Norbornadiene precursor **6** and model compound **7**

For the norbornadiene precursor, we thought of the bis(iodonium) derivative **5**, recently described by Stang and Zhdankin (Scheme 4).[13] This compound is easily prepared and can undergo either copper-mediated nucleophilic substitutions yielding dihalo- or dicyanonorbornadiene,[14] or palladium/copper ethynylation with an alkynylstannane, affording a family of new enediyne-containing molecules.[15]

Only two reports were found in which the dithienylperfluorocyclopentene photochromic group is used as a synthon (i.e., a diboronic acid[6e]or a dibromide[16]): the usual strategy is to prepare the derivatives by the interaction of a suitably substituted 3-lithiothiophene and perfluororocyclopentene in the final step.[5,6a–6d]

A convenient precursor of the diiodinated synthon **9** is the bis(5-trimethylsilyl) derivative of 1,2-bis(2′-methylthien-3′-yl)perfluorocyclopentene (**8**), the synthesis of which was described by Irie.[16] In marked contrast to the difficulty of the analogous bromination reaction,[16] the electrophilic trimethylsilyl *ipso* substitution with ICl as iodinating agent smoothly afforded the previously unknown diiodo derivative **9** in virtually quantitative yield. (Scheme 5).



8 **9**

Scheme 5. Dithienylethene precursor

Crystallization from acetonitrile afforded crystals suitable for an X-ray study; an ORTEP diagram is given in Figure 2.

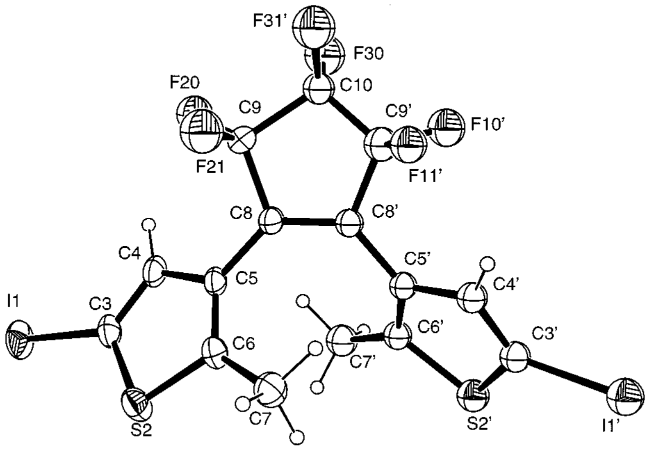


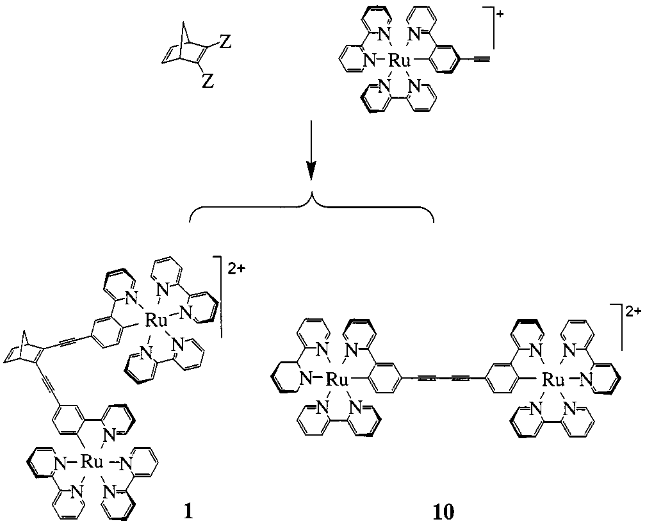
Figure 2. ORTEP plot of **9** with 30% probability displacement ellipsoids; the atoms with a superscript prime are related to those without superscript by a crystallographic twofold axis running though the middle of the C(8)–C(8′) bond; the nonplanar perfluorocyclopentene ring is partially disordered and only one conformer is shown here for clarity (bond lengths in Å, torsion angle in °): I1–C3 2.072(5), C3–C4 1.351(7), C4–C5 1.438(6), C5–C6 1.368(7), C3–S2 1.706(6), S2–C6 1.732(5), C5–C8 1.465(6), C8–C8′ 1.362(8); C6–C5–C8–C8′ 42(1)

Compound **9** exhibits pseudo-C_2 symmetry. The general conformation is transoid, that is, the methyl groups of the thiophene rings are above and below the plane of the perfluorocyclopentene ring, as Irie et al. observed for the related 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene.[17] This conformation is adapted for the cyclization reaction which can occur with relatively small movements.[17] The angle between the thiophene rings and the perfluorocyclopentene ring is 42°. The perfluorocyclopentene ring is not strictly planar, and thus the molecule exists in two conformations with statistical disorder (only one is shown in Figure 2). The bond lengths are in agreement with an electronic structure made up of two thiophene rings linked essentially by a single bond to perfluorocyclopentene. There appears to be little or no conjugation between the three rings.

Final Coupling

In the case of norbornadiene derivatives, difficulties were experienced in the stannylation of the alkyne functionality,[18,19] so we attempted a direct coupling with the bis(iodinane) **5**. Dinuclear complexes were readily obtained.

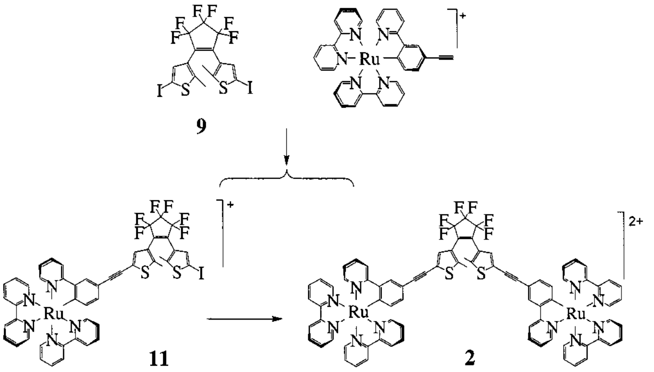
Unfortunately, a careful mass-spectrometry analysis showed that the desired complex **1** was systematically contaminated with the butadiyne derivative **10**, resulting from an oxidative coupling reminiscent of the Glaser reaction, despite drastic precautions against atmospheric oxygen contamination. Suspecting the iodinane **5** to be the necessary oxidizer,[20] we thought of using the expectedly less reactive diiodonorbornadiene **6**. Adapting literature coupling conditions to this substrate,[21] we were able to prepare the desired complex **1** in 40% yield (Scheme 6).



1 **10**

Scheme 6. Norbornadiene dinuclear complexes

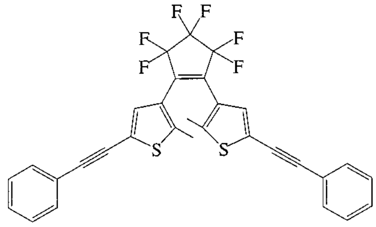
In the case of the dithienylethene derivative, ethynylation occurred at room temperature in DMF under Sonogashira's conditions with $Pd(PPh_3)_4$ as catalyst source,[10,22] yielding the dinuclear complex **2**, albeit in moderate yield (20%). The major by-product was the mononuclear complex **11** (30%) which could be, if needed, converted into the dinuclear complex **2** by the same reaction conditions (Scheme 7).



9 **11** **2**

Scheme 7. Dithienylethene complexes

All the dinuclear complexes were purified by preparative thin layer chromatography on silica, with a mixture of toluene and acetonitrile as eluent. However, it was found that crude complexes had to be deposited in CH_2Cl_2 to get proper separation (vide infra). These complexes, isolated as hexafluorophosphates, were identified by conventional analytical techniques.[23]



12a

Scheme 8. Model compound **12a**

Finally, for comparison purposes, the model compound **12a** (Scheme 8), in which the conjugated part is similar to the one of **2a**, was synthesized from **9** and phenylacetylene.[24]

Electrochemistry and Intervalence Electron Transfer in the Native Forms 1 and 2a

The cyclic voltammograms of **1** and **2a** exhibit a single reversible oxidation wave at 0.50 and 0.53 V (MeCN) vs SCE, respectively, corresponding to the oxidation of both ruthenium(II) sites. However, as in similar complexes with large metal−metal separations, this does not preclude the generation of appreciable concentrations of the mixed valence $Ru^{II}-Ru^{III}$ form during partial oxidation.[2] Conproportionation constants (K_c) for the equilibria between the $Ru^{II}-Ru^{II}$, $Ru^{III}-Ru^{III}$ and $Ru^{II}-Ru^{III}$ (mixed valence forms) were obtained by differential pulse voltammetry. K_c was found to be 13 for **1** and to be 11 for **2a**, corresponding to ca. 65% of the mixed-valence form at half-oxidation. These K_c values compare well with the ones observed for complexes of similar length.[2c]

An estimation of the electronic coupling parameter V_{ab} from the intervalence band characteristics is possible through Hush's Equation [Equation (1)][3,25] where $\bar{\nu}$ is the band position, $\Delta\bar{\nu}_{1/2}$ is the full width at half-maximum, and ε_{max} is the maximum extinction coefficient, while R_{MM} is the metal−metal distance.

$$V_{ab} = \frac{2.05\ 10^{-2}\sqrt{\bar{\nu}\ \Delta\bar{\nu}_{1/2}\ \varepsilon_{max}}}{R_{MM}} \tag{1}$$

In the case of **1**, the progressive oxidation (either chemical or electrochemical) revealed an intervalence transition in the 1300−2000-nm range. After correction for the conproportionation equilibrium, and deconvolution of the mixed-valence spectrum to extract the profile of the intervalence transition, according to a method already published,[2a,2d] the intervalence band parameters were obtained (Table 1). The V_{ab} parameter is found to be 0.068 eV. It is interesting to compare this with the similar complex with dicyanonobornadiene as a bridge and pentaammineruthenium as end groups, for which the coupling (0.023 eV) was three times less.[4] This shows the advantage of cyclometalated units as redox groups.

In the case of **2a** (where ruthenium atoms are initially in oxidation states II−II), the progressive oxidation to the

Table 1. Intervalence band parameters for compounds **1** and **2b**

Compound	K_c	$\tilde{\nu}$ [cm^{-1}]	$\Delta\tilde{\nu}_{1/2}$ [cm^{-1}]	ε [mol^{-1} L cm^{-1}]	R_{MM} [Å]	V_{ab} [eV]
1	13±2	5500±200	5000±300	3460±200	11.1	0.068±0.005
2b	12±2	7400±500	5000±300	1400±100	23.4	0.025±0.003

III−III fully oxidized form could be achieved easily and was found to be reversible. During oxidation, a band near 850 nm kept appearing; it is assigned to a ligand-to-metal charge transfer transition. No intervalence band was observed, regardless of the oxidation method [electrochemical with concentration, $c = 4{\cdot}10^{-4}$ M, or chemical with bis(pyridyl)phenyliodonium triflate with concentration, $c = 6{\cdot}10^{-5}$ M, see below].

Photochemistry

Photoisomerizations were undertaken for complexes **1** and **2a**, with the aim of generating either a less conjugated form (norbornadiene to quadricyclane isomerization of **1**) or a more conjugated form (photocyclization of the dithienylethene derivative **2a**).

In the case of **1**, irradiations at 254 and 365 nm either in methanol or acetonitrile, monitored by ^{1}H-NMR spectroscopy, did not produce isomerization to quadricyclane. Experiments on the simpler compound 1,2-bis(phenylethynyl)norbornadiene (**7**) did not result in photoisomerization either. Thus, it seems that for norbornadiene, the extension of conjugation due to the phenylethynyl parts is responsible for the lack of photochemical reactivity, probably by quenching the excited state of the norbornadiene part. Such negative effects of the conjugation length were described elsewhere.[26]

Irradiation of **2a** in MeCN or CH_3OH at different wavelengths (405, 313, 365, and 254 nm) was first followed by UV/Vis spectroscopy. A broad band appeared at 670 nm, which corresponds to the photocyclized isomer, according to similar examples.[6b][6e] The highest intensity at the photostationary state was obtained with 254-nm irradiation, and all following studies were performed at this wavelength. Since the other bands in the UV/Vis spectra did not disappear (see below), another technique was necessary to measure the degree of conversion into the closed form. We found that for concentrations of ca. $2{\cdot}10^{-4}$ mol L^{-1} it was possible to monitor the reaction (in CD_3OD) by both UV/Vis and ^{1}H-NMR spectroscopy, in the latter case the signals of the methyl protons closest to the newly created bond were used. During irradiation, the sharp singlet at $\delta = 1.98$, corresponding to methyl protons of the open form **2a**, decreased and was progressively replaced by a signal at $\delta = 2.21$, attributed to the methyl protons of the closed form. The relative integration of the two methyl signals showed that a photostationary state was reached after two hours of irradiation, the closed form **2b** concentration reaching 75% of the initial complex content. Since conversions up to 100% were reported for similar systems,[6] the incomplete isomerization in our case is probably related to the persistence of an absorption for the closed form at all wavelengths, due to the organometallic part. Thus, in contrast to other photochromic compounds of this family, it is not possible to find a wavelength for which only the open form **2a** would be excited.

Since the photochemical ring closure of **2a** was not complete, a purification step was necessary to obtain the spectroscopic behavior of the pure closed form **2b**. However, the conditions described above, involving thin-layer chromatography with a toluene/acetonitrile mixture as eluent failed; the two isomers migrated as a single and stretched spot. It was recently shown[27] that chromatographic elution of ionic compounds was made difficult because of some streaking of the bands. This was attributed to partial ion exchange between the ion pairs and the stationary phase. To force this equilibrium toward ion-pairing, and since dichloromethane gave the best results as deposition solvent, we chose to saturate the TLC plate with an excess of KPF_6. Despite their relatively small structural differences, separation of the two isomers **2a** and **2b** could be achieved: elution with a dichloromethane/ethyl acetate/pyridine mixture revealed a pink band (**2a**) followed by a blue band (**2b**) which migrated slightly more slowly (R_F = 0.40 and 0.34 for **2a** and **2b**, respectively). The ^{1}H-NMR spectrum of the blue product (Figure 3) agreed with structure **2b**, and showed, in particular, the displacement of the thiophene protons upon cyclization.

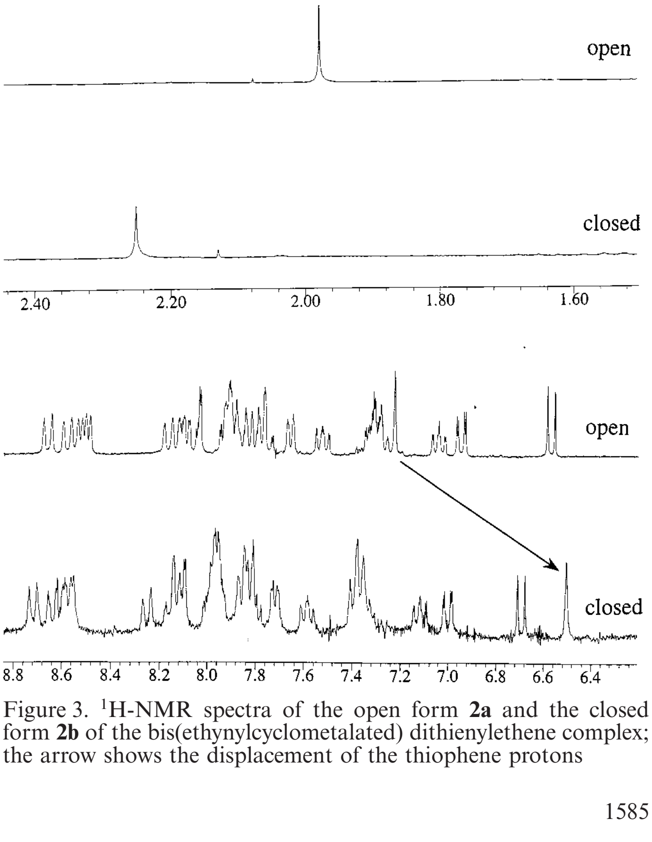


Figure 3. ^{1}H-NMR spectra of the open form **2a** and the closed form **2b** of the bis(ethynylcyclometalated) dithienylethene complex; the arrow shows the displacement of the thiophene protons

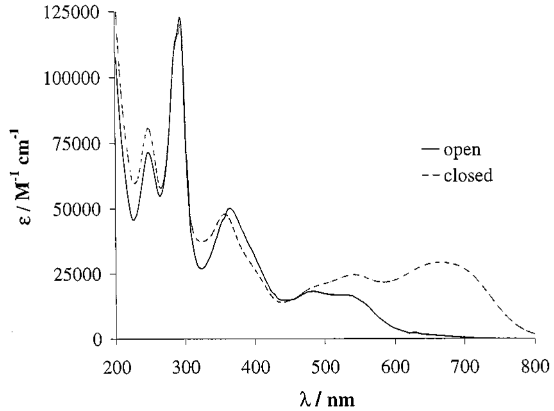


Figure 4. UV/Vis spectra of the open form **2a** and the closed form **2b** of the bis(ethynylcyclometalated) dithienylethene complex

The closed form did not revert thermally when kept for several hours in the dark. The back-reaction, that is, ring reopening, could be observed when irradiation was performed in the red part of the spectrum, with an incandescence lamp with a Kodak red filter excluding radiation below 600 nm.

The UV/Vis spectra of **2a** and **2b** are shown in Figure 4. Upon photocyclization, the UV/Vis spectrum is modified mainly in the red region, with the broad 670-nm peak rising. In the rest of the spectrum, only weak changes are observed, with a small decrease of some bands (see Figure 4). The extinction coefficient at 670 nm for the closed form is 29700 $\mathrm{mol^{-1}\ L\ cm^{-1}}$. This high value can be related to the presence of donor substituents,[28] in our case the cyclometalated ruthenium(II) units, and also to the length of the conjugated system.

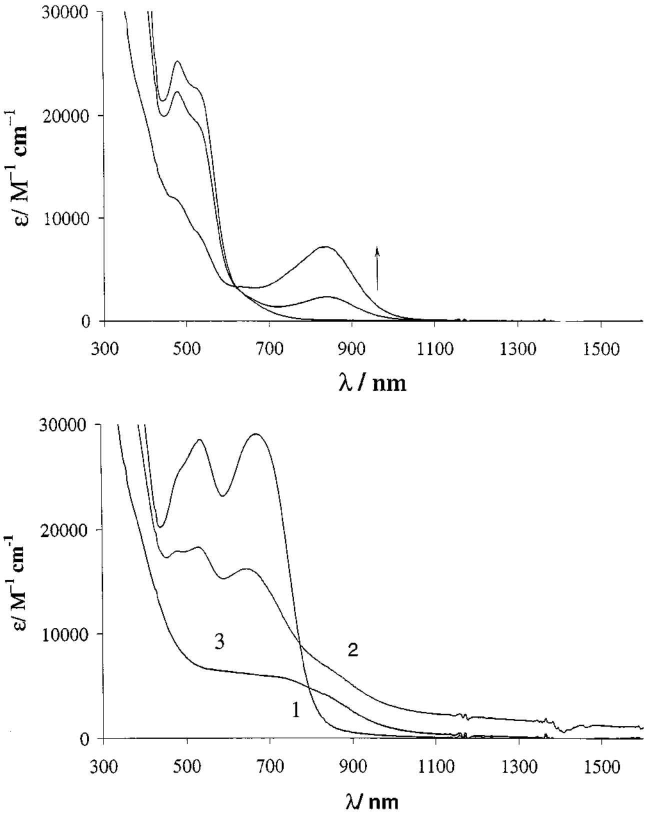


Figure 5. Spectra obtained during oxidation with bis(pyridyl)-phenyliodonium; top: *open* form **2a**; bottom: *closed* form **2b** exhibiting an intervalence absorption in the 1000−1500 nm range; total concentration: $5.7 \cdot 10^{-5}$ mol·L^{-1}; path length: 1 cm; 1: initial spectrum; 2: spectrum at half-oxidation; 3: spectrum of the fully oxidized solution

Electrochemistry and Intervalence Transition of 2b

The closed form **2b** gives rise to a single oxidation wave at 0.52 V (MeCN) vs SCE, corresponding to the oxidation of both ruthenium atoms. Differential pulse voltammetry yields $K_c = 12$.

The oxidation of **2b**, particularly by controlled-potential electrolysis, was not a simple process. During oxidation, the characteristic band of the closed form of the photochromic core, near 670 nm, decreased, suggesting a major alteration of the structure. Furthermore, after complete oxidation, a reduction by hydrazine did not restore the characteristic color and spectrum of **2b** in its reduced form, but instead a spectrum very close to the one of **2a**. Thus, during oxidation, a ring reopening occurred, and the final product was the oxidized form of **2a**.[29] (Incidentally, the same oxidation-induced ring reopening was also observed with the mononuclear **11b** complex.)

We found that the reopening during electrolysis was in fact a relatively slow reaction (half-reaction time ca. 5−10 min), consecutive to the oxidation step. Thus, it was conceivable to quench it with a faster oxidation procedure than controlled-potential electrolysis, the latter being limited by mass transport between the electrode and the bulk solution. After systematic search of chemical oxidation procedures, we chose an oxidation by the triflate salt of bis(pyridyl)phenyliodonium, formally containing iodine(III).[30] Interestingly, in our case, this reagent reacted instantaneously, did not generate acidic species (which would be harmful for the cyclometalated moieties), and the by-products are merely iodobenzene and pyridine. Finally, both the reagent and by-product (iodobenzene) are almost nonabsorbent in the visible and near-IR regions.

Upon chemical oxidation of pure **2b**, obtained from chromatography, we observed the decrease of the 670-nm band and the rising and subsequent decay of a weak absorption in the near-infrared, behavior characteristic of intervalence transitions (Figure 5, bottom). [The decrease of the 670-nm band comes from the fact that the ruthenium(II) donor groups, which increase the extinction coefficient of the closed form, [28] are no longer present.] In a control experiment, no near-IR absorption was obtained by oxidation of the monometallic complex **11a**, neither with the open form itself nor with the closed form **11b**; this suggests that the near-IR absorption in **2b** is indeed linked to the bimetallic nature of the complex.

To obtain the parameters for Hush's equation, after correction for the conproportionation equilibrium ($K_c = 12$), the spectrum was deconvoluted according to a procedure already described,[2d] to separate the intervalence band from the tail of the nearby more intense band located near 900 nm. Although no true maximum was observed for the intervalence band, spectral simulation showed that a band exists. Additional evidence for an intervalence absorption was provided by the reproducibility of the results, and the typical increase followed by a decrease upon oxidation. The resulting parameters of the intervalence band are reported in Table 1. With the use of R_{MM} = 23.4 Å, from molecular modeling methods,[31] V_{ab} = 200 cm^{-1} (0.025 eV). By contrast, as said above, nothing was observed in the case of **2a** (Figure 5, top).

To understand the electronic mechanism of the coupling, an extended Hückel evaluation of V_{ab} in both **2a** and **2b** was performed. We showed elsewhere that this method is sufficient for obtaining realistic values of the electronic coupling and that it allows qualitative discussions.[2a] The geometries of **2a** and **2b** were first minimized by molecular mechanics.[31] Then molecular orbitals were computed by the extended Hückel method,[32] and V_{ab} was obtained from the "dimer splitting" procedure.[2a] For **2b**, a coupling of 0.021 eV was obtained versus 0.003 eV for **2a**. The former value is consistent with the observed coupling, while the latter explains the disappearance of the intervalence transition, since a 7-fold reduction in V_{ab} should result in a ca. 50-fold (i.e., 7^2) reduction in the extinction coefficient. In chemical terms, for **2a**, the useful part of the bridge (ignoring sulfur contributions) is made up of a nonconjugated octatriene, while in **2b**, it can be considered to be a conjugated octatetraene. Interestingly, values of V_{ab} in the 0.02-eV range have already been observed for conjugated systems with four double bonds and metal−metal distances near 20 Å.[2d] A more complete discussion of the spatial extension and properties of the orbitals involved in the electron transfer for such compounds is given elsewhere.[33]

The extended Hückel calculation also rationalizes the behavior of **2b** upon oxidation. While in **2a**, the ruthenium d orbitals are well separated from other molecular orbitals with mainly ligand character, so that the oxidation is truly metal-centered, in **2b**, a filled orbital of the ligand has moved up and appears at an energy very close to metal orbitals. Thus, although the oxidation bears primarily on the metal (as shown by the electrochemical behavior: **2a** is oxidized reversibly at 0.53 V, while the model compound **12a** is oxidized *irreversibly* at 1.04 V[24]), it is relatively easy to partially depopulate a *ligand* orbital by oxidation. Because this ligand orbital is bonding between carbon atoms C-5′ and C-5″ (see Figure 1b), its depopulation should favor the reopening. In this respect, the oxidation process is somewhat analogous to the photochemical excitation.

Conclusion

The general synthetic strategy of using palladium-catalyzed ethynylation reactions between a substituted acetylene and an electrophilic sp^2-hybridized carbon atom proved to be versatile and could be adapted for the present purpose. Compounds with two redox groups linked by a photoisomerizable bridge were obtained, but their behavior differed markedly with respect to the bare photochromic parts. In particular, the extension of conjugation could suppress photoisomerization (**1**) or make it nonquantitative (**2a**), probably because the additional conjugated parts and the redox groups can act as energy sinks. Such an effect was also reported elsewhere.[26]

Despite these difficulties, we found two interesting features associated with the same molecule (**2a/2b**): full photoinduced electron transfer between two metal units, and reversible photochromism. The intervalence transition could be switched completely "on" or "off". The order of magnitude of the electronic coupling in both forms was correctly reproduced by an extended Hückel calculation. Compounds **2a** and **2b** allowed a fundamental study of switching (in the electrical sense) at the molecular level.

Experimental Section

Starting Materials: Reagents were of commercial grade. THF was dried with Na/benzophenone, CH_2Cl_2 with CaH_2, and MeCN with molecular sieves. Amines were used as received. Preparative TLC plates were purchased from Merck. Compound **4** was synthesized according to ref.[9] Octafluorocyclopentene was purchased from Interchim. Bis(iodonium)norbornadiene (**5**), diiodonorbornadiene (**6**), bis(phenylethynyl)norbornadiene (**7**) were synthesized according to literature procedures. For **8**, the procedure in ref.[16] was adapted: Octafluorocyclopentene was added to a ca. 0.2 M solution of 4-lithio-5-methyl-2-trimethylsilylthiophene in THF at −80 °C, and the mixture was allowed to warm up over 5 h. Compound **8** was obtained after chromatography (SiO_2, pentane) and recrystallization (MeCN), the yield was 50% on a gram scale. All the reactions and handling of the compounds sensitive to UV light were carried out in the dark.

Perfluoro-1,2-bis(2-iodo-5-methylthien-4-yl)cyclopentene (9): A solution of **8** (150 mg, 0.29 mmol) and iodine monochloride (190 mg, 1.17 mmol) in CH_2Cl_2 (10 mL) was stirred at −5 °C for 2 h. After solvent evaporation, the residue was purified by column chromatography (basic Al_2O_3, pentane) to give 165 mg of **9** as a waxy solid in 90% yield. M.p. 96 °C. − ^1H NMR: (250 MHz, $CDCl_3$, 20 °C, TMS): δ = 7.2 (s, 1 H), 1.9 (s, 3 H). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 250 MHz, 20 °C): δ = 147.7 (C-5′), 136.0,(C-3′), 135.2 (C-2′), 126.6 (C-4′), perfluorocyclopentene (multiplets) 111.7, 115.7, 119.9, 14.3 (CH_3). − ^{19}F NMR (CD_3OD, 200 MHz, 20 °C, external CF_3COOH as reference): δ = −31.7 to −31.9 (m, 2 F), −53.5 to −53.6 (m, 1 F). − MS (CI, NH_3); *m/z* (%): 620.0 (100). − $C_{15}H_8S_2F_6I_2{\cdot}CH_3CN$ (619.8): calcd. C 30.88, H 1.68, S 9.70; found C 30.86, H 1.50, S 9.53.

Ethynylcyclometalated Compound 3: A solution of **4** (150 mg, 0.19 mmol) and potassium *tert*-butoxide (25 mg, 0.22 mmol) in 5 mL of dry, oxygen-free THF was stirred at reflux temp. for 2 h. After the solvent was cooled and removed, the residue was taken up in dichloromethane and the filtered solution was concentrated, yielding **3** as an amorphous solid. The reaction was quantitative. − ^1H NMR (250 MHz, CD_3CN, 20 °C, TMS): δ = 3.27 (s, 1 H), 6.47 (d, *J* = 7.8 Hz, 1 H), 6.91 (dd, *J* = 7.7, 1.6 Hz, 1 H), 6.9 (td, *J* = 6.0, 1.4 Hz, 1 H), 7.21−7.26 (m, 3 H), 7.43 (td, *J* = 7.0, 1.2 Hz, 1 H), 7.60 (dd, *J* = 4.0, 1.0 Hz, 2H), 7.69−7.87 (m, 7 H), 7.96−8.08 (m, 3 H), 8.33 (dd, *J* = 8.0, 3.0 Hz, 2 H), 8.40 (d, *J* = 8.1 Hz, 1 H), 8.46 (d, *J* = 8.1 Hz, 1 H). − MS (FAB, NBA); *m/z* (%): 592 (100) $[M - PF_6]^+$. − $C_{33}H_{24}N_5PF_6Ru$ (736): calcd. C 53.81, H 3.28, N 9.51; found C 53.78, H 3.76, N 8.71.

Bis(ethynylcyclometallated) Norbornadiene Complex 1: Diiodonorbornadiene (30.9 mg 0.09 mmol), $Pd(PPh_3)_4$ (10 mg, 0.05 equiv.), CuI (10 mg, 0.3 equiv.) and finally 1 mL of diisopropylamine were added to 2 mL of a DMF solution containing 0.19 mmol of **3**. The solution was stirred at room temp under argon for 10 h. The solvent was then removed in vacuo and the crude product was purified by chromatography on a silica gel preparative plate (eluent: toluene/acetonitrile 60:40), with desorption by a concentrated solution of ammonium hexafluorophosphate in MeCN). Yield: 59 mg (40%). – ^{1}H NMR: (250 MHz, CD_3CN, 20 °C, TMS): δ = 2.17–2.19 (m, 1 H), 2.30–2.32 (m, 1 H), 3.70 (br. s, 2 H), 6.51 (d, J = 7.9 Hz, 2 H), 6.85–6.97 (m, 6 H), 7.10–7.25 (m, 6 H), 7.40–7.53 (m, 4 H), 7.58–7.86 (m, 14 H), 7.94 (sd, J = 1.5 Hz, 2 H), 7.97–8.03 (m, 6 H), 8.29–8.35 (m, 4 H), 8.38 (d, J = 8.2 Hz, 2 H), 8.46 (d, J = 8.2 Hz, 2 H). – MS (ES); *m/z*: 1417 $[M - PF_6]^+$, 859 $[M - 2PF_6 - (Ru(bpy)_2)]^+$, 790 $[M - 2PF_6 - (Ru(bpy)_2) - Cp]^+$, 636 $[M - 2PF_6]^{2+}$. – $C_{73}H_{52}N_{10}P_2F_{12}Ru_2{\cdot}3H_2O$ (1615): calcd. C 54.28, H 3.62, N 8.67; found C 54.21, H 3.88, N 8.09.

Mono- and Bis(ethynylcyclometalated) Dithienylethene Complexes in Their Open Forms 11a and 2a: The reaction was carried out with 55.8 mg (0.09 mmol) of **9** and was worked up in a manner identical to that described above for the synthesis of **1**. Yield 32 mg (20%) of **2a** and 33 mg (30%) of **11a**.

11a: ^{1}H NMR: (250 MHz, CD_3OD, 20 °C, TMS): δ = 1.96 (s, 3 H), 1.99 (s, 3 H), 6.56 (d, J = 7.7 Hz, 1 H), 6.95 (dd, J = 7.7, 1.7 Hz, 1 H), 7.04 (td, J = 6.7, 1.1 Hz, 1 H), 7.20 (s, 1 H), 7.28–7.35 (m, 4 H), 7.42 (d, J = 5.5 Hz, 1 H), 7.52 (td, J = 7.8, 1.6 Hz, 1 H), 7.65 (dd, J = 5.1, 1.0 Hz, 1 H), 7.72–7.97 (m, 6 H), 8.04 (sd, J = 1.9 Hz, 1 H), 8.08–8.13 (m, 2 H), 8.18 (d, J = 7.9 Hz, 1 H), 8.52 (dd, J = 8.4, 3.7 Hz, 2 H), 8.58 (d, J = 7.9 Hz, 1 H), 8.66 (d, J = 8.1 Hz, 1 H). – ^{19}F NMR (CD_3OD, 200 MHz, 20 °C, external CF_3COOH as reference): δ = −31.7 to −31.9 (m, 2 F), −53.5 to −53.6 (m, 1 F). – MS (ES); *m/z*: 1084.1 $[M - PF_6]^+$. – UV/Vis (MeCN): λ_{max} (ε, $M^{-1}{\cdot}cm^{-1}$) = 482 (12300), 364 (30800), 294 (81100), 248 (62000) nm. – $C_{48}H_{31}N_5PF_{12}S_2IRu{\cdot}2EtOH$ (1321.5): calcd. C 47.28, H 3.28, N 5.30; found C 47.94, H 2.97, N 5.31.

2a: ^{1}H NMR (250 MHz, CD_3OD, 20 °C, TMS): δ = 1.98 (s, 6 H), 6.57 (d, J = 7.9 Hz, 2 H), 6.96 (dd, J = 7.9, 1.6 Hz, 2 H), 7.04 (td, J = 6.4, 1.0 Hz, 2 H), 7.24 (s, 2 H), 7.26–7.37 (m, 6 H), 7.52 (td, J = 6.4, 1.2 Hz, 2 H) 7.65 (dd, J = 5.1, 1.0 Hz, 2 H), 7.72–7.96 (m, 14 H), 8.01 (sd, J = 1.6 Hz, 2 H), 8.08–8.19 (m, 6 H), 8.52 (dd, J = 8.2, 3.9 Hz, 4 H), 8.58 (d, J = 8.1 Hz, 2 H), 8.66 (d, J = 7.9 Hz, 2 H). – ^{19}F NMR (CD_3OD, 200 MHz, 20 °C, external CF_3COOH as reference): δ = −31.7 to −31.9 (m, 2 F), −53.5 to −53.6 (m, 1 F). – MS (ES); *m/z*: 1693 $[M - PF_6]^+$, 774 $[M - 2PF_6]^{2+}$. – UV/Vis in MeOH: λ_{max} (ε, $M^{-1}{\cdot}cm^{-1}$) = 480 (20600), 366 (50000), 295 (139000), 247 nm (84100). – $C_{81}H_{54}N_{10}P_2F_{18}S_2Ru_2{\cdot}6H_2O$ (1944): calcd. C 50.00, H 3.42, N 7.20; found C 49.86, H 3.14, N 6.93.

Bis(ethynylcyclometalated) Dithienylethene Complex in Its Closed Form 2b: Compound **2a** was converted into **2b** on a preparative scale as follows: An efficiently stirred solution of **2a** (16 mg) in 10 mL of acetonitrile or methanol was irradiated in a quartz vessel with two standard TLC-visualization UV lamps at 254 nm for 12 to 24 h. To the resulting mixture, 0.05 mL of hydrazine and 5 mg of NH_4PF_6 were added, and the solution was concentrated to dryness. The solid was dissolved in dichloromethane and subjected to preparative TLC chromatography on silica gel plates previously immersed in a saturated aqueous KPF_6 solution for 1 h and then dried in an oven overnight. Elution of the plate (eluent: dichloromethane/ethyl acetate/pyridine, 100:100:1) was carried out with careful protection from light. Washing of the silica with a mixture of dichloromethane/ethanol/triethylamine (91:8:1) readily provided desorption of the band corresponding to **2b** (6.5 mg).

2b: ^{1}H NMR (250 MHz, CD_3OD, 20 °C, TMS): δ = 2.21 (s, 6 H), 6.46 (s, 2 H), 6.65 (d, J = 7.4 Hz, 2 H), 6.80 (d, J = 7.5 Hz, 2 H), 7.04–7.10 (m, 2 H), 7.24–7.40 (m, 6 H), 7.48–7.59 (m, 2 H), 7.68 (d, J = 4.5 Hz, 2H), 7.74–8.00 (m, 14 H), 8.03–8.13 (m, 6 H), 8.21 (d, J = 7.9 Hz, 2 H), 8.46–8.61 (m, 6 H), 8.68 (d, J = 8.1 Hz, 2 H). – UV/Vis in MeOH: λ_{max} (ε, $M^{-1}{\cdot}cm^{-1}$) = 670 (29700), 545 (24800), 358 (48500), 295 (123000), 248 nm (82000). – $C_{81}H_{54}N_{10}P_2F_{18}S_2Ru_2{\cdot}10H_2O$ (2016): calcd. C 48.22, H 3.70, N 6.94; found C 48.31, H 3.47, N 6.49.

X-ray Crystal Structure of 9: Crystals were obtained by cooling of a saturated solution in acetonitrile, and were mounted on an Enraf Nonius Kappa CCD diffractometer. Mo-K_α (λ = 0.71073 Å) radiation was used and the temperature was 293 K. The space group was monoclinic *C*2/*c*; a = 20.7183(5) Å, b = 9.0480(5) Å, c = 11.9644(4) Å, β = 120.987(2)°, V = 1922.8(9) Å^3, Z = 4. Structure determination was performed with direct methods (SIR 92),[34] from 2470 reflections, of which 1810 with $I > 3\sigma(I)$ were used for refinement against F^2 (CRYSTALS).[35] Non-hydrogen atoms were treated anisotropically except for disordered atoms (C10 and F). H atoms (isotropic) were placed from difference Fourier maps and were not refined. Final values: R = 5.17%, Rw = 7.26%; residual electron density: −0.8, +1.2 e/Å^3. Drawings were made with ORTEP III.[36] Crystallographic data (excluding structure factors) for the structure reported in this paper were deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136201. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (UK) [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Photochemistry: For analytical investigations, photochemical irradiations of **2a** were performed in 2-mm or 1-cm quartz cells placed in front of either a standard TLC-visualization UV lamp (365 and 254 nm), or an optical system combining a medium-pressure Mercury lamp and interference filters (405, 365, and 313 nm). For the reopening reaction of **2b**, an incandescence lamp with a red filter was used. The solutions were stirred either with a small magnetic bar (1-cm cells), or by the cell being turned upside down every minute (2-mm cells incompletely filled under argon to imprison a bubble). Concentrations were in the 10^{-5} mol L^{-1} range (1-cm cells). For the combined UV/Vis/NMR experiment in CD_3OD at 254 nm, the concentration was $2{\cdot}10^{-4}$ mol L^{-1} (2-mm cells). After irradiation of the photostationary state, the solution (ca. 0.6 mL) was transferred to the NMR tube. Preparative photochemistry took place in a quartz vessel as described above.

Electrochemistry: Electrochemical techniques were performed with an AUTOLAB PC-controlled potentiostat. The reference electrode was a saturated calomel electrode (SCE) isolated from the solution by a double frit system. The solvent was acetonitrile and the supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. For cyclic voltammetry, the working electrode was a Pt disk (diameter 1 mm), and the scan rate 0.1 V·s^{-1}. Differential pulse voltammetry was performed with a Metrohm rotating platinum electrode (1000 rev/min) with pulses of 70 ms duration and 25 mV amplitude. For controlled potential electrolysis, the working electrode was a platinum grid, and the anodic and cathodic compartments were separated by a additional frit.

Iodine(III) Reagent: The reported preparation[30] starts from iodobenzene diacetate. However, the commercial reagent gave unsatisfactory results. Thus, it was prepared from iodobenzene, acetic anhydride, and hydrogen peroxide according to ref.[37] Then iodobenzene diacetate was converted into the triflate salt of bis(pyridyl)phenyliodonium by reaction with trimethylsilyl trifluoromethanesulfonate.[30] The obtained whitish solid was kept under argon at −20 °C.

For oxidation experiments, in a typical run, a $5.7{\cdot}10^{-5}$ mol L^{-1} solution of **2a** in anhydrous MeCN was prepared. A volume of 2.5 mL of this solution was started with, and the oxidation was performed in a 1-cm cell by addition of a solution of the iodine(III) reagent ($3.0{\cdot}10^{-2}$ mol·L^{-1} in MeCN) with a micropipette. Full oxidation was found to occur for 26 μL, at which the spectrum of the $Ru^{III}-Ru^{III}$ species was obtained. In a second experiment, half the above quantity (i.e., 13 μL) was added, and the absorption spectrum, corresponding to the mixed-valence species in conproportionation equilibrium, was immediately recorded. For the closed form **2b**, oxidation was performed as above on 1 mL of a $2.6{\cdot}10^{-4}$ M solution in a 5-mm cell.

Calculations: Compounds **2a** and **2b** were minimized[31] with the universal force field[38] modified with the following parameters: 350 kcal mol^{-1} Å^{-2} and 2.05 Å for Ru−N bonds, 350 kcal mol^{-1} Å^{-2} and 2.02 Å for Ru−C bonds. Since the energy was almost insensitive to a rotation around the acetylenic bonds, the thiophene rings and the phenyl groups were made coplanar to avoid rotational disorder. This gave molecules with only one element of symmetry, a C_2 axis. Molecular orbitals were computed by the extended Hückel method, with the CACAO program[32] with Ru(4d) orbital energies set at −11.0 eV. The V_{ab} parameters were extracted from the energy splitting between two orbitals with strong weights on metal atoms and opposite symmetries with respect to the C_2 axis of the molecules. Due to the low symmetry around the metal sites, it turned out that for each molecules *two* such couples of orbitals were found: one corresponding to an interaction propagating through the phenyl ring of the phenylpyridine ligand, and another corresponding to an interaction through the pyridine ring. Since the two couplings V_{phen} and V_{pyr} were of the same order of magnitude, they were combined by Equation (2).

$$V_{ab} = \sqrt{V_{phen}^2 + V_{pyr}^2} \qquad (2)$$

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[23] Due to the chirality of the organometallic group (Λ or Δ configuration), the complexes are obtained as mixtures of stereoisomers such as ΛΛ, ΔΛ and ΔΛ for **2a**. However, the chiral centers are generally sufficiently far apart for their steric interaction to be negligible, so that the chirality of the two metal centers can be considered to be independent. Moreover, in similar examples involving $Ru(bipy)_2$-like terminal units, no consequences of the chirality of the metal centers were reported, neither on the NMR spectra (J. Bolger, A. Gourdon, E. Ishow, J.-P. Launay, *Inorg. Chem.* **1996**, *35*, 2937), nor on the electrochemical and spectroscopic behavior (M. J. Powers, T. J. Meyer, *J. Am. Chem. Soc.* **1980**, *102*, 1289; A. C. Benniston, V. Goulle, A. Harriman, J.-M. Lehn, B. Marczinke, *J. Phys. Chem.* **1994**, *98*, 7798). See also the review: R. J. Crutchley, *Adv. Inorg. Chem.* **1994**, *41*, 273, and references therein. Thus, the stereochemical aspects are not considered in the rest of this paper.

[24] ^1H NMR (250 MHz, CD_3OD, 20 °C) of **12a**: δ = 2.02 (s, 3 H), 7.34 (s, 1 H), 7.40−7.46 (m, 3 H), 7.58−7.60 (m, 2 H). Electrochemistry: irreversible oxidation at 1.04 V vs SCE in MeCN. Colorless "open" compound **12a** undergoes photocyclization upon irradiation with UV light, to give the "closed" cobalt-blue isomer **12b**. For a $1.6{\cdot}10^{-5}$ M solution in MeCN, the photostationary state is reached within 25 s (cf. 30 s for **8**). UV/Vis in MeCN: λ_{max} (nm) (ε [M^{-1} cm^{-1}]): *open* form (**12a**): 306 (61250); *closed* form (**12b**): 604 (21900).

[25] In this expression, V_{ab}, $\bar{\nu}$, and $\Delta\bar{\nu}_{1/2}$ are in cm^{-1}, ε_{max} in mol^{-1} L cm^{-1}, and R_{MM} is in Å. The proportionality factor

0.0205 comes from (i) the definition of the oscillator strength f in terms of experimental quantities, (ii) the relation of f with the transition moment μ_{tr} (P. W. Atkins, *Physical Chemistry*, 4th ed., Oxford University Press, Oxford, **1990**, pp. 503−504), and (iii) the expression of μ_{tr} in the particular case of intervalence transitions, according to Hush.[3] The literal expression of this factor is $[3\,h\,C\,\varepsilon_0(\ln 10)/4\,\pi^2\,N_A\,e^2]^{1/2}\,(\pi/\ln 2)^{1/4}$ where h is Planck's constant, C is the velocity of light, ε_0 is the permittivity of a vacuum, N_A is Avogadro's number, and e is the elementary charge; a value of $6.513\cdot10^{-12}$ is obtained in SI units. Converted into the more common non-SI units, the result is $6.513\cdot10^{-12} \times (1000)^{1/2}\cdot10^8$, i.e., 0.0205.

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