6402 *Organometallics* **2009,** *28,* 6402–6409
DOI: 10.1021/om900396b

ORGANOMETALLICS
Article

Syntheses and Properties of Binuclear Ruthenium Vinyl Complexes with Dithienylethene Units as Multifunction Switches

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Received May 14, 2009

A series of binuclear ruthenium vinyl complexes with dithienylethene units, $[RuCl(CO)(PMe_3)_3]_2$-(μ-CH=CH-DTE-CH=CH) (**5a**, **5b**), $[RuCl(CO)(Py)(PPh_3)_2]_2$($\mu$-CH=CH-DTE-CH=CH) (**6a**, **6b**), $[RuTp(CO)(PPh_3)]_2$(μ-CH=CH-DTE-CH=CH) (**7a**, **7b**), and $[RuCl(CO)(PMP)]_2$(μ-CH=CH-DTE-CH=CH) (**8a**, **8b**) (DTE = 1,2-bis(2-methylthiophen-3-yl)cyclopentene; 1,2-bis(2-methylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene), have been prepared. The respective products have been characterized by elemental analyses, NMR spectrometry, and UV/vis spectrophotometry. The structures of **3a** and **5b** have been established by X-ray crystallography. It is revealed that the binuclear ruthenium vinyl complexes with dithienylethene units show photochromic behavior, but their absorption spectra, cyclization/cycloreversion quantum yields, and the efficiency of the photochromic process are highly dependent on the central switching units and the ancillary ligands attached to the metal. Electrochemical studies have shown that the open-ring isomers of the metal complexes are triggered, either by light or electricity, to convert to their closed forms. It has clearly been demonstrated that these complexes represent a class of light- and electrotriggered multifunctional switch molecules featuring electrochromism, electrocyclization, and photo/electrotuning of the electronic communication.

Introduction

Linear compounds with redox-active organometallic termini linked by π-conjugated organic ligands are of current interest as candidates for "molecular wires" that allow electron transfer to occur along their molecular backbones. Particular attention has been focused on investigation of bimetallic polyynediyl complexes $\{M\}$-$(C\equiv C)_m$-$\{M\}^{1-8}$ and polyylenediyl complexes $\{M\}$-$(CH=CH)_m$-$\{M\}^{9}$ because of their facile accessibility and high efficiency for electronic delocalization.

In order to assemble a photoswitchable organometallic molecular wire, Akita[10] and Rigaut[11] introduced a switching unit, such as a dithienylperfluorocyclopentene moiety (DTE), into carbon-rich bimetallic complexes $\{M\}$-(μ-$C\equiv C$-$C\equiv C$)-$\{M\}$ (M = Fe, Ru) and thereby synthesized bimetallic complexes $\{M\}$-(μ-$C\equiv C$-DTE-$C\equiv C$)-$\{M\}$. The closed isomers of the bimetallic complexes, obtained upon irradiation with UV light,

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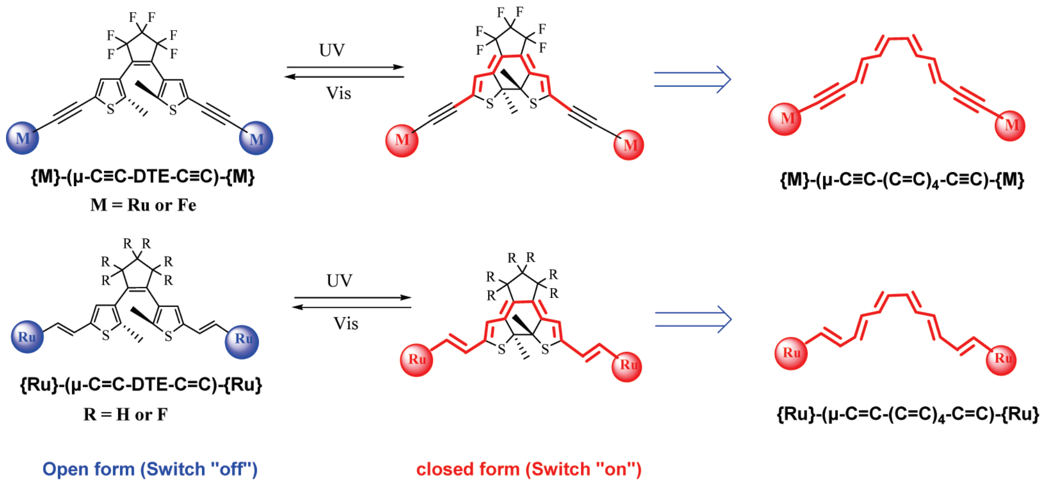
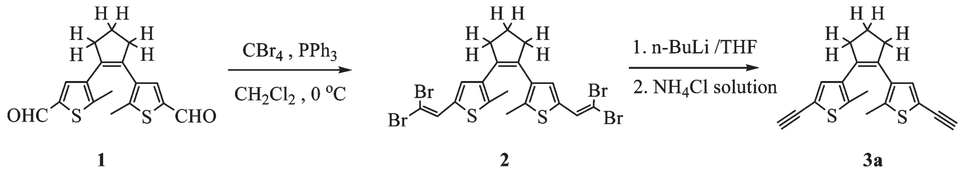
Scheme 1



Scheme 2



had extended π-conjugated systems similar to the structure of {M}-(μ-C≡C-(C=C)$_4$-C≡C)-{M} (Scheme 1) and exhibited electronic coupling between the metal centers. In the work described in this paper, we have introduced a dithienylethene unit (DTE = 1,2-bis(2-methylthiophen-3-yl)cyclopentene; 1,2-bis(2-methylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene) into bimetallic dienediyl complexes {Ru}-(μ-C=C-C=C)-{Ru} and have thereby synthesized binuclear ruthenium vinyl complexes incorporating dithienylethene units {Ru}-(μ-C=C-DTE-C=C)-{Ru}, of which the closed isomers have a similar structure to that of {Ru}-(μ-C=C-(C=C)$_4$-C=C)-{Ru} (Scheme 1). It has been found that the binuclear ruthenium vinyl complexes with dithienylethene units exhibit switching behavior that is triggered by either photo- or electrochemical stimuli. We have also found that the photophysical and electrochemical properties of these molecules can be easily tuned by introducing different central switching bridges or by attaching different ancillary ligands to the metals.

Results and Discussion

Preparation and Characterization of Binuclear Ruthenium Vinyl Complexes with Dithienylethene Units. 1,2-Bis(5-ethynyl-2-methylthiophen-3-yl)cyclopentene (**3a**) was obtained from the corresponding dialdehyde through the Corey−Fuchs reaction[12] (Scheme 2). 1,2-Bis(5-formyl-2-methylthiophen-3-yl)cyclopentene (**1**) was first reacted with CBr_4/PPh_3 at 0 °C, furnishing the dibromoalkene derivative **2** in good yield. Elimination of HBr was best achieved using an excess of *n*BuLi in THF at room temperature, and the resulting anion was quenched with aqueous NH_4Cl solution to give the terminal diacetylene **3a** in 63% yield. The terminal diacetylene **3b** was prepared following the published procedure.[13] Compounds **2** and **3a** were characterized by ^{1}H and

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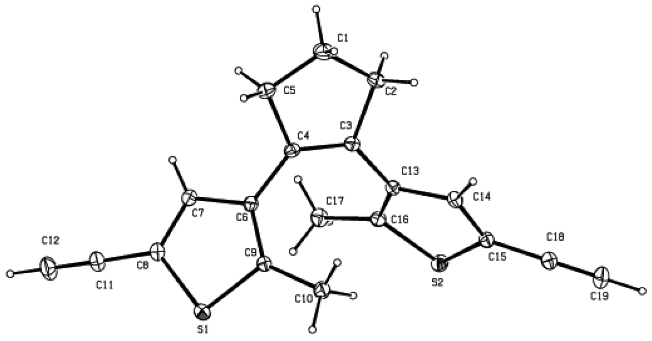

Figure 1. Molecular structure of **3a**.

^{13}C NMR spectrometry. The structure of **3a** was also verified by X-ray crystallography (Figure 1).

The general synthetic route for the preparation of binuclear ruthenium vinyl complexes (**4**−**8**) is outlined in Scheme 3. The terminal diacetylenes **3** were treated with [RuHCl(CO)(PPh$_3$)$_3$] to give the insertion products [RuCl(CO)(PPh$_3$)$_2$]$_2$(μ-CH=CH-DTE-CH=CH) (DTE = 1,2-bis(2-methylthiophen-3-yl)cyclopentene; 1,2-bis(2-methylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene) (**4**), which were isolated as solids (brown for **4a**, light green for **4b**). These compounds have been characterized by NMR. The ^{31}P NMR spectra of complexes **4** in CDCl$_3$ showed a singlet at δ = 32.01 ppm (**4a**) or δ = 31.48 ppm (**4b**), which is typical of [RuCl((*E*)-CH=CHR)(CO)(PPh$_3$)$_2$].[14] The ^{1}H NMR spectra of complexes **4** in CDCl$_3$ displayed the Ru-CH signal at δ = 7.95 ppm (**4a**) or δ = 8.03 ppm (**4b**), these chemical shifts being similar to those of complexes [RuCl(CO)(PPh$_3$)$_2$]$_2$(μ-(CH=CH)$_n$)[9] and [RuCl(CO)(PPh$_3$)$_2$]$_2$(μ-CH=CH-Ar-CH=CH),[15] as well as singlet signals due to the methyl groups attached to the thiophene rings at δ = 1.69 and 1.63 ppm in **4a** and **4b**, respectively. The five-coordinate complexes **4** were found to be air-sensitive, especially in solution.

Several related six-coordinated complexes (**5**−**8**) were prepared from complexes **4**. Reactions of **4** with trimethylphosphine (PMe$_3$), pyridine (Py), KTp (Tp = hydridotris(pyrazolyl)borate), and 2,6-(Ph$_2$PCH$_2$)$_2$C$_5$H$_3$N (PMP) gave the corresponding six-coordinated complexes [RuCl(CO)(PMe$_3$)$_3$]$_2$(CH=CH-DTE-CH=CH) (**5**), [RuCl(CO)(Py)(PPh$_3$)$_2$]$_2$(CH=CH-DTE-CH=CH) (**6**), [RuTp(CO)(PPh$_3$)]$_2$(CH=CH-DTE-CH=CH) (**7**), and [RuCl(CO)(PMP)]$_2$(CH=CH-DTE-CH=CH) (**8**), respectively. These complexes have been characterized by NMR spectrometry and elemental analysis. The PMe$_3$ ligands in **5** are meridionally coordinated to ruthenium, as indicated by an AM$_2$ pattern in the ^{31}P{^{1}H} NMR spectrum. The ^{1}H NMR spectrum (in CDCl$_3$) of **5a** features the two Ru-CH proton signals at δ = 7.53 ppm (**5b**, δ = 7.72 ppm), this chemical shift being similar to that found in [RuCl(CO)(PMe$_3$)$_3$]$_2$(μ-(CH=CH)$_n$).[9] The two vinylic protons (Ru-CH=CH) are in a *trans* geometry, and the acetylene is *cis* inserted into the Ru−H bond, as confirmed by the X-ray structure of **5b** (Figure 2). The presence of the thiophene rings is indicated by the ^{1}H NMR spectrum, which features characteristic singlet signals at δ = 6.31 ppm for **5a** and 6.50 ppm for **5b**, respectively. The other six-coordinated complexes (**6**−**8**) display similar chemical shifts in their spectra, in accordance with those of related ruthenium complexes that have been reported previously.[9]

X-ray Structures of 3a and 5b. The molecular structures of **3a** and **5b** were verified by X-ray crystallography and the crystallographic details are given in Table 1. The molecular structures of **3a** and **5b** are depicted in Figures 1 and 2, respectively. It is evident that the thiophene moieties of the two compounds are packed in an antiparallel conformation in the crystalline phase, a conformation that is crucial for the compound to exhibit photochromic and photoinduced properties.[16] In **3a**, the two planar thiophene ring systems have similar geometries, with dihedral angles between the cyclopentene ring and the adjacent thiophene rings of 48.38° (S1/C6−C9) and 45.41° (S2/C13−C16). The intramolecular distance between the two reactive carbons C(9)−C(16) is 3.559 Å, which is short enough for the cyclization reaction to take place, as photochromic reactivity usually appears when the distance between the reactive carbon atoms is less than 4.2 Å.[17] In the hexafluorocyclopentene rings of **5b**, the F atoms of the CF$_2$ groups are disordered, and two distinct conformations could be modeled with occupancies of 0.53 and 0.47, respectively. The distance between the two reactive carbons C(8)−C(8a) is 3.610 Å, which is similar to that in the nonmetalated derivative **3a**, indicating that the attachment of the bulky organoruthenium fragments does not induce a significant conformational change in the central DTE unit. The carbon atoms of the thiophene ring and the vinyl moiety are nearly coplanar, with a dihedral angle of 1.66°, which somewhat extends the π-conjugated system. The two Ru centers are related by a pseudo-C_2 rotation axis, and the two olefinic double bonds are in a *trans* configuration. The overall geometry about the two ruthenium centers in **5b** closely resembles that in bimetallic ruthenium complexes of the type [RuCl(CO)(PMe$_3$)$_3$]$_2$(μ-(CH=CH)$_n$).[9a,d,f]

Photochromic Behavior of Binuclear Ruthenium Vinyl Complexes with Dithienylethene Units. The photochromic behavior of the binuclear ruthenium vinyl complexes (**5**−**8**) was examined by means of UV/vis spectrophotometry and compared to that of the free DTE molecules **3**. All of the synthesized dithienylethene compounds **3** and **5**−**8** undergo reversible photochromic reactions in dichloromethane upon alternating irradiation with UV light (302 nm) and visible light (λ > 420 nm) using cutoff filters. The absorption maxima and extinction coefficients of the open- and closed-ring isomers of dithienylethene compounds **3** and **5**−**8** in dichloromethane are summarized in Table 2.

Figure 3 shows the spectral changes of compound **5b** dissolved in dichloromethane (2.0 × 10^{-5} mol dm^{-3}), the original absorption maximum of which appeared at 316 nm. Upon irradiation with light of wavelength 302 nm for 20 s, the system reached a photostationary state and the colorless solution of the open-ring isomer turned dark blue, showing a new band in the visible region at 622 nm due to the formation of the closed isomer. This blue color was bleached by

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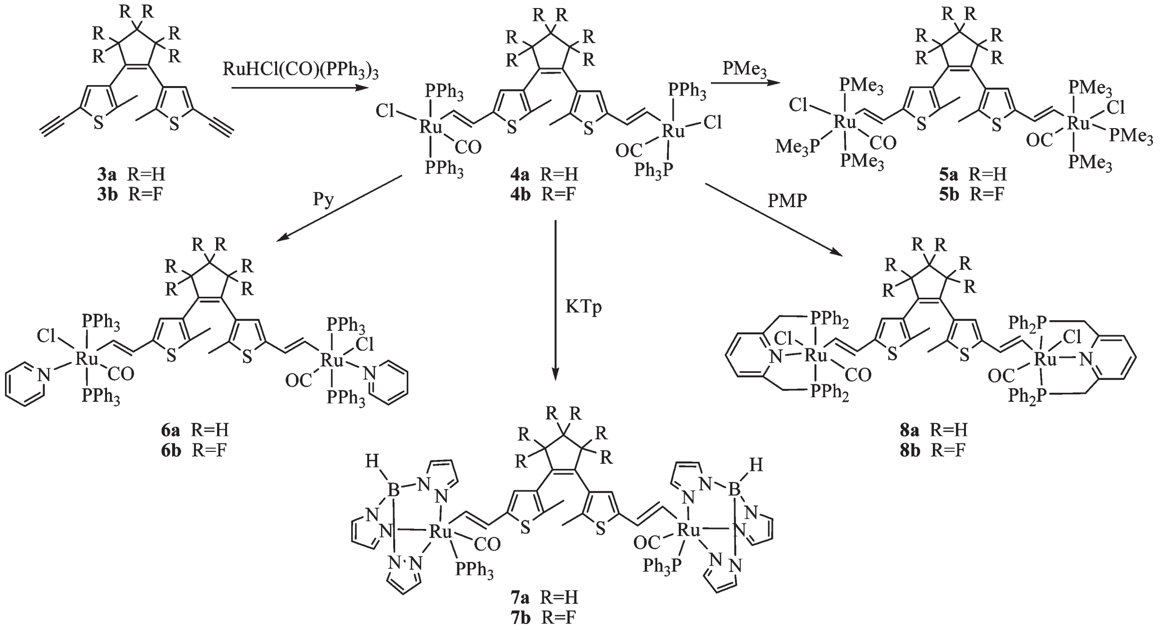
Scheme 3



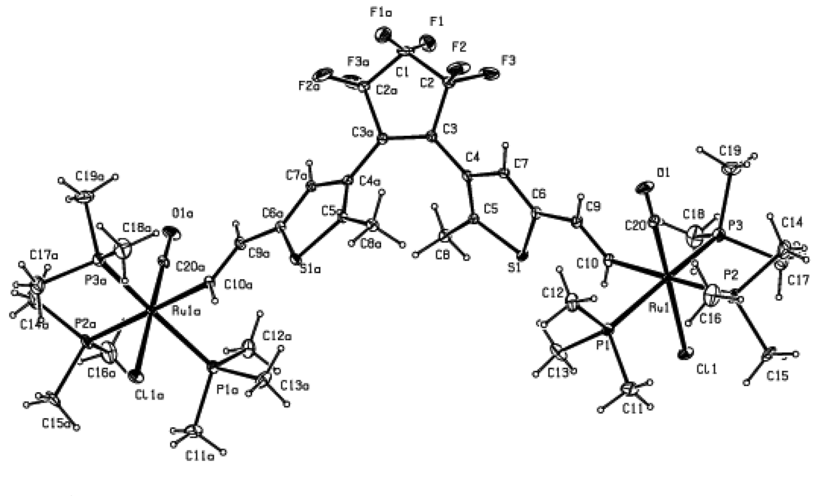


Figure 2. Molecular structure of **5b**.

subsequent irradiation with visible light, the system reverting to the original open-ring state within 15 min. The separation of closed isomer **5bC** and opened isomer **5bO** is not successful by column chromatograpy or HPLC. However, the characteristic shifts of their Me and thiophene were observed in the ^{1}H NMR ($CDCl_3$, 1.0×10^{-3} mol dm^{-3}). The ^{1}H NMR signal for the methyl groups attached to the thiophene rings appeared at 1.81 ppm for **5bO** and 1.97 ppm for **5bC**, and the ^{1}H NMR signal for the protons attached to the thiophene rings appeared at 6.50 ppm for **5bO** and 5.82 ppm for **5bC**, respectively. The ^{31}P NMR signal for the opened isomer (**5bO**) and closed isomer (**5bC**) are at −6.91 and −18.52 ppm for **5bO** and −8.10 and −19.68 ppm for **5bC**, respectively. The ^{1}H NMR signal for the proton on thiophene rings and ^{31}P NMR signal for **5bC** appeared at higher field compared to that of **5bO**, but the ^{1}H NMR signal of the methyl for **5bC** appeared at lower field. Similar shift changes have been observed in the NMR for other dithienylethene compounds (Table S1Supporting Information).

The ratio between closed isomer and opened isomer at the photostationary state of **5b**, which can be measured by ^{1}H NMR spectra, is 90:10 (**5bC**/**5bO**). Similar spectral changes have been observed for other dithienylethene compounds. The content of their closed isomers at their UV photostationary states is 35−80% (Table S 1). The cyclization/cycloreversion cycle number has been examined in CH_2Cl_2 at room temperature, as shown in Figure S2. Diarylethene metal complex **5b** was irradiated alternatively with 302 nm and visible light (λ > 420 nm), respectively. The cycle number characteristics indicated that ∼40% of **5b** has been destroyed after 10 repeated cycles. This may be ascribed to degradation resulting from the CO ligands.

As shown in Table 2, the absorption maxima of the open-ring and closed-ring forms were dependent on the central switching units at the reaction centers and the ancillary ligands attached to the metal. The closed isomers of the hexahydro switches (**5a**−**8a**) turned dark red, while the hexafluoro switches (**5b**−**8b**) became dark blue upon UV irradiation. This was because the absorption maxima of the hexafluoro compounds were bathochromically shifted to the region 622−642 nm, while those of the hexahydro compounds were only shifted to 530−548 nm.

Table 1. Crystal Data, Data Collection, and Refinement Parameters for 3a and 5b

	3a	5b
formula	$C_{19}H_{16}S_2$	$C_{51}H_{94}C_{12}F_6O_2P_6Ru_2S_2$
fw	308.44	1376.24
temp(K)	292(2)	200(2)
cryst syst	monoclinic	orthorhombic
space group	$P2(1)/c$	$P2(1)2(1)2$
a (Å)	10.7458(11)	15.5384(5)
b (Å)	7.6990(8)	25.2257(9)
c (Å)	20.227(2)	8.5389(3)
α (deg)	90.00	90
β (deg)	102.002(2)	90
γ (deg)	90.00	90
V (Å^{-3})	1636.9(3)	3347.0(2)
Z	4	2
D_{calcd} (g cm^{-3})	1.252	1.366
cryst size (mm)	0.20 × 0.10 × 0.10	0.30 × 0.25 × 0.20
F(000)	648	1428
diffractometer	KappaCCD	KappaCCD
radiation	Mo Kα	Mo Kα
abs coeff (mm^{-1})	0.316	0.788
θ range (deg)	1.94−27.50	1.54−25.00
hkl range	−13 to 13; −7 to 9; −26 to 23	−18 to 18; −27 to 30; −10 to 9
total no. of rflns	9478	35 496
no. of unique rflns	3710	5906
no. of obsd rflns ($I > 2\sigma(I)$)	2787	5754
no. of restraints/params	0/192	15/343
a, b for W^a	0.0790, 0.0865	0.065, 4.9674
final R	0.0515	0.0526
R_w	0.1339	0.1312
R (all data)	0.0693	0.0540
R_w (all data)	0.1433	0.1321
goodness of fit/F^2	1.055	1.202
largest diff peak, hole (e Å^{-3})	0.345, −0.208	1.059, −0.565

[a] $W = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, where $P = (F_o^2 + F_c^2)/3$.

Metalation led to notable differences in both the absorption maxima and quantum yields for these two different systems. The quantum yields of the dithienylethene compounds in photocyclization and photocycloreversion were measured in dichloromethane according to the literature method.[18] As shown in Table 2, the photocyclization quantum yield of **3a** (Φo-c = 0.35) was found to be higher than that of **3b** (Φo-c = 0.19). However, the photocyclization quantum yields of the hexahydro systems (**5a**−**8a**) decreased to 0.11−0.14 when the metal groups were attached to the reaction centers. In contrast, the photocyclization quantum yields of the hexafluoro systems (**5b**−**8b**) increased to 0.26−0.58. Similar dramatic changes in the photocycloreversion quantum yields were also observed in the cycloreversion reactions (Table 2). It is worth noting that the efficiencies of the cyclization and cycloreversion depended on the metal and ancillary ligands. The metal complexes **5**−**8** reached photostationary states more efficiently than the free DTE molecules **3** (i.e., ca. 60 s for **3b**; ca. 20 s for **5b**, **6b**; and 12 s for **7b**, **8b**). However, more significant differences were observed for the reverse ring-opening process, whereby the metal complexes **5**−**8** reverted to their open isomers more slowly than the metal-free species (i.e., ca. 2 min for **3b** and within 20 min for **5b**−**8b**). This suggests that metalation has a significant impact on the stability of the ring-closed isomers. This is in accordance with the findings of Akita's group on how different metal species influence the efficiencies of cyclization and cycloreversion.[10b]

Electrochemical Properties of the Binuclear Ruthenium Vinyl Complexes with Dithienylethene Units. The extent of the interaction between the two metal termini in the two isomeric forms was examined by electrochemical methods. The redox behavior of the binuclear complexes **5**−**8** (1.0×10^{-3} mol dm^{-3} in CH_2Cl_2) has been investigated by cyclic voltammetry (CV) and square-wave voltammetry (SWV) techniques using 0.1 mol dm^{-3} nBu$_4$NPF$_6$ as the supporting electrolyte. The electrochemical data of complexes **5**−**8** are shown in Table 3.

Typical changes in the cyclic voltammograms of **5b** before and after irradiation with 302 nm light are shown in Figure 4. At a scan rate of 0.1 V s^{-1}, a broad oxidation wave was observed at 0.57 V, which was attributed to a one-step 2e process of the two noncommunicating ruthenium centers in the open isomer. Upon UV (302 nm) irradiation, two new waves appeared at less positive potentials. The two new well-separated redox features were reversible and were located at 0.02 and 0.17 V, respectively; they could be ascribed to the oxidation of Ru^{II,II} to Ru^{II,III} and then to Ru^{III,III}. The $\Delta E_{1/2}$ value (0.15 V) of the closed isomer is smaller than the $\Delta E_{1/2}$ value (0.20 V) of $[RuCl(CO)(PMe_3)_3]_2(\mu\text{-}(CH{=}CH)_7)$.[9e] This process of **5b** can be viewed in terms of communication between the metal centers being switched "on" and "off" by UV/visible light.

Further investigations by controlled-potential electrolysis were performed on **5b** at 0.60 V in the same way as reported by Irie[19] and Rigaut.[11] Figure 3 shows the absorption spectral changes accompanying the electrolysis of a solution of the open-ring isomer of **5b** in dichloromethane containing tetrabutylammonium hexafluorophosphate at 0.60 V (vs Ag/Ag$^+$). The electrolysis process was completed in 917 s. **5b** became blue and showed the new absorption band at 634 nm due to the formation of the closed isomer (**5bC**$^{2+}$). When the blue solution was irradiated with visible light, the blue color disappeared. As Branda[20] and Feringa[21] reported, this voltammogram suggests that **5b** undergoes an oxidative cyclization reaction. That is to say, the cyclization reaction of **5b** can be induced not only by photoirradiation but also by electrochemical oxidation.

Similar behavior was noted for the other metal derivatives (**5a**, **6a**, **7a**, **6b**, and **7b**). From the electrochemical data of complexes collected in Table 3, it can be seen that changes of the central cyclopentene units and the ligands bound to Ru have large effects on the oxidation potentials. For metal complexes with perfluorocyclopentene as the spacer (**5b**−**7b**), the oxidation potentials (E_p) before UV irradiation and the $\Delta E_{1/2}$ values after UV irradiation are higher than those of their perhydro counterparts (**5a**−**7a**). These $\Delta E_{1/2}$ values indicate that the hexafluoro DTE bridges facilitate stronger electronic communication between the two metal centers. Varying the ligands bound to the Ru centers,

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Table 2. Photochromic Parameters for Compounds 3 and Complexes [RuCl(CO)(PMe$_3$)$_3$]$_2$(μ-CH=CH-DTE-CH=CH) (5−8) in CH$_2$Cl$_2$ at 2.0 × 10^{-5} mol dm^{-3}

	λ_{max}/nm (ε /L mol^{-1} cm^{-1})		Φ^a	
	open	closed^b	Φo-c	Φc-o^c
3a (R = H)	262(30 800)	518(8900)	0.35	0.79
3b (R = F)	260(35 000)	379(3750); 577(4000)	0.19	0.23
5a (R = H, L = PMe$_3$)	319(33 100)	542(5950)	0.12	0.10
5b (R = F, L = PMe$_3$)	316(47 136)	390(22 423); 622(17 956)	0.58	0.85
6a (R = H, L = Py)	319(33 100)	551(10 300)	0.12	0.24
6b (R = F, L = Py)	318(42 600)	405(26 500); 640(23 800)	0.26	0.41
7a (R = H, L = Tp)	333(22 800)	530(3550)	0.11	0.085
7b (R = F, L = Tp)	329(12 550)	411(7450); 642(7900)	0.33	0.39
8a (R = H, L = PMP)	322(23 000)	548(5500)	0.14	0.43
8b (R = F, L = PMP)	324(22 550)	409(17 200); 641(17 250)	0.40	0.38

^{a} Quantum yields of cyclization (Φo-c) and cycloreversion (Φc-o). ^{b} Mersured by irradiation with UV light (302 nm). ^{c} Measured by irradiation light (λ = 550 nm).

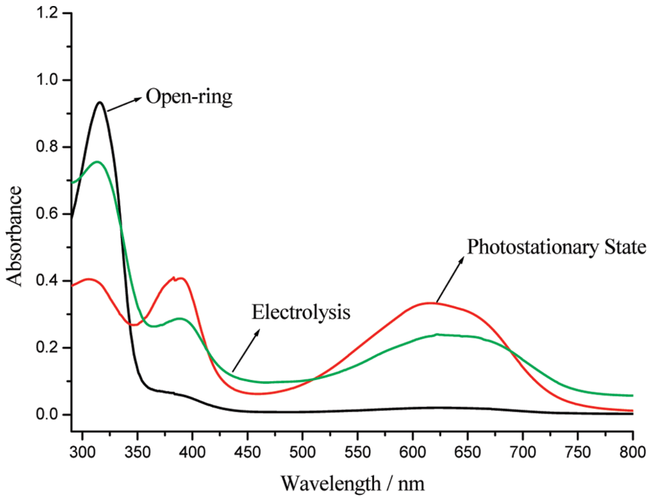

Figure 3. (a) Absorption spectral change of **5b** under irradiation with 302 nm light or electrolysis (CH$_2$Cl$_2$: [**5b**] = 2.0 × 10^{-5} mol dm^{-3}). Open-ring (black line), photostationary state (PSS) (red line), and electrolysis at 0.60 V for 917 s (Ag/Ag$^+$) (green line).

Table 3. Electrochemical Data for complexes 5−8^a

	open	closed		
compound	E_p	$E_{1/2}$(A)	$E_{1/2}$(B)	$\Delta E_{1/2}{}^b$
5a (R = H, L = PMe$_3$)	0.26	−0.31	−0.17	0.14
5b (R = F, L= PMe$_3$)	0.57	0.020	0.17	0.15
6a (R = H, L= Py)	0.20	−0.46	−0.29	0.17
6b (R = F, L= Py)	0.41	−0.016	0.21	0.23
7a (R = H, L= Tp)	0.18	−0.41	−0.25	0.16
7b (R = F, L= Tp)	0.40	−0.020	0.17	0.19
8a (R = H, L = PMP)	0.16	−0.38		
8b (R = F, L = PMP)	0.32	−0.047		

^{a} Potential data were determined in CH$_2$Cl$_2$ containing 1 mmol dm^{-3} compound and 0.1 mol dm^{-3} Bu$_4$NPF$_6$. The Ag/Ag$^+$ electrode (internal solution: 0.01 mol dm^{-3} AgNO$_3$ + 0.1 mol dm^{-3} Bu$_4$NPF$_6$ in acetonitrile; salt bridge: 0.1 mol dm^{-3} Bu$_4$NPF$_6$ in CH$_2$Cl$_2$) was used as a reference. ^{b} $\Delta E_{1/2}$ = $E_{1/2}$(B) − $E_{1/2}$(A) denotes the potential difference between redox processes A and B.

the $\Delta E_{1/2}$ values for complexes **5a−7a**, **6b**, and **7b** are 0.14, 0.17, 0.16, 0.23, and 0.19 V, respectively. However, upon UV irradiation, a new broad oxidation wave was observed only at −0.38 V for **8a** and −0.047 V for **8b**, respectively. The investigations by controlled-potential electrolysis were performed on **5a−8a** and **6b−8b** at 0.20−0.45 V. The results show that all of complexes undergo an oxidative cyclization reaction.

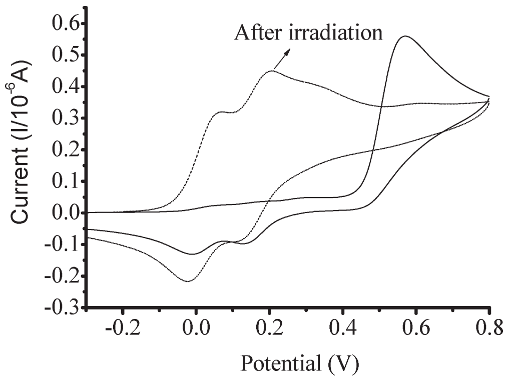

Figure 4. Cyclic voltammograms of **5b** in CH$_2$Cl$_2$ containing nBu$_4$NPF$_6$ (0.1 mol/L), before (solid line) and after (dashed line) irradiation with 302 nm light at the scan of 100 mV/s. Potentials are given relative to the Ag/Ag$^+$ standard.

Conclusions

A series of binuclear ruthenium vinyl complexes containing two kinds of photochromic DTE functional groups have been prepared and characterized spectroscopically and crystallographically. It has been demonstrated that the binuclear ruthenium vinyl complexes with dithienylethene units show photochromic behavior and that their absorption spectra, their cyclization/cycloreversion quantum yields, and the efficiencies with which they undergo the photochromic process are highly dependent on the central switching units and the ancillary ligands attached to the metal. Electrochemical studies have shown that the open-ring isomers of the metal complexes could be triggered either by light or electricity to convert to their closed forms. It has clearly been demonstrated that these complexes represent a class of light- and electrotriggered multifunctional switch molecules displaying electrochromism, electrocyclization, and photo/electrotuning of the electronic communication.

Experimental Section

General Materials. All manipulations were carried out under a nitrogen atmosphere by using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium-benzophenone (diethyl ether, THF) or calcium hydride (dichloromethane, hexane). The starting materials RuHCl(CO)(PPh_3)$_3$,[22] KTp,[23] 2,6-(Ph_2PCH_2)$_2$$C_5H_3$N(PMP),[24] 1,2-bis-(5-formyl-2-methylthiophen-3-yl)cyclopentene (**1**)[13] and 1,2-bis-(5-ethynyl-2-methylthiophen-3-yl)perfluorocyclopentene (**3b**)[13] were prepared according to the literature methods. Elemental analyses (C, H, N) were performed by the Microanalytical Services, College of Chemistry, CCNU. ^{1}H, ^{13}C, and ^{31}P NMR spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz). ^{1}H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. UV–vis spectra were obtained on U-3310 UV spectrophotometer.

Preparation of 1,2-Bis(5-dibromoethenyl-2-methylthiophen-3-yl)cyclopentene (2). To a CH_2Cl_2 solution (15 mL) of CBr_4 (5.3 g, 16 mmol) cooled to 0 °C in an ice-bath was added dropwise PPh_3 (8.4 g, 32 mmol) dissolved in CH_2Cl_2 (15 mL) over 30 min. The reaction mixture was stirred at 0 °C for 10 min, and then a solution of 1,2-bis(5-formyl-2-methylthiophen-3-yl)cyclopentene (**1**) (1.26 g, 4 mmol) in 10 mL of CH_2Cl_2 was added over 10 min via cannula. After that the solution was stirred at 0 °C for 1 h, and 50 mL of H_2O was added. The resulting mixture was extracted by CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtrated, and concentrated under rotary evaporation. The residue was purified by silica gel column chromatography using hexane as the eluent to give 1.8 g of the product. Yield: 75%. Anal. Calcd for $C_{19}H_{16}Br_4S_2$: C, 36.33; H, 2.57. Found: C, 36.12; H, 2.46. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.92 (s, 6H, CH_3), 2.04 (m, 2H, CH_2), 2.76(t, J = 7.4 Hz, 4H, CH_2), 6.88 (s, 2H, thiophene-H), 7.45 (s, 2H, CH=CBr_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.46, 22.82, 38.32, 85.47, 130.79, 131.24, 133.94, 134.32, 134.99, 137.11.

Preparation of 1,2-Bis(5-ethynyl-2-methylthiophen-3-yl)cyclopentene (3a). To a THF solution (40 mL) of **2** (1.8 g, 3.0 mmol) was added dropwise *n*BuLi (4.8 mL, 2.5 M in hexane); 5 min later, the reaction mixture was quenched with aqueous NH_4Cl solution and extracted with CH_2Cl_2. The organic layer was dried with Na_2SO_4 and concentrated under rotary evaporation. The residue was purified by silica gel column chromatography using hexane as the eluent to give 0.6 g of the product. Yield: 65%. Anal. Calcd for $C_{19}H_{16}S_2$: C, 73.98; H, 5.23. Found: C, 73.77; H, 5.50. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.89 (s, 6H, CH_3), 2.04 (m, 2H, CH_2), 2.74 (t, J = 7.4 Hz, 4H, CH_2), 3.27 (s, 2H, C≡CH), 6.96 (s, 2H, thiophene-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.22, 22.82, 38.47, 77.22, 80.60, 117.88, 134.09, 134.47, 135.43, 137.23.

General Synthesis of Complexes [RuCl(CO)(PPh_3)$_2$]$_2$(CH=CH-DTE-CH=CH) (4). To a suspension of RuHCl(CO)(PPh_3)$_3$ (0.152 g, 0.16 mmol) in CH_2Cl_2 (10 mL) was slowly added a solution of **3** (0.10 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 30 min to give a red solution. The reaction mixture was filtered through a column of Celite. The volume of the filtrate was reduced to ca. 5 mL under vacuum. Addition of hexane (50 mL) to the residue produced a solid (**4a**, red; **4b**, brown), which was collected by filtration, washed with hexane, and dried under vacuum.

4a. Yield: 130 mg, 77%. ^{31}P NMR (160 MHz, $CDCl_3$): δ 32.01 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.69(s, 6H, CH_3), 1.94–2.00 (m, 2H, CH_2), 2.67 (t, J = 7.6 Hz, 4H, CH_2), 5.47–5.50 (m, 2H, thiophene-CH=), 5.89 (s, 2H, thiophene-H), 7.08–7.58 (m, 60H, Ph), 7.93–7.96 (m, 2H, RuCH=).

4b. Yield: 137 mg, 76%. ^{31}P NMR (160 MHz, $CDCl_3$): δ 31.48 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.63 (s, 6H, CH_3), 5.46–5.49 (m, 2H, thiophene-CH=), 6.05 (s, 2H, thiophene-H), 7.25–7.56 (m, 60H, Ph), 8.01–8.05 (m, 2H, RuCH=).

General Synthesis of Complexes [RuCl(CO)(PMe_3)$_3$]$_2$(CH=CH-DTE-CH=CH) (5). To a solution of complex **4** (0.2 mmol) in CH_2Cl_2 (30 mL) was added a 1 M THF solution of PMe_3 (2.0 mL, 2.0 mmol). The reaction mixture was stirred for 15 h. The solution was filtered through a column of Celite. The volume of the filtrate was reduced to ca. 2 mL under vacuum. Addition of hexane (30 mL) to the residue produced a solid (**5a**, light red; **5b** light green), which was collected by filtration, washed with hexane, and dried under vacuum.

5a. Yield: 180 mg, 82%. Anal. Calcd for $C_{39}H_{74}Cl_2O_2P_6Ru_2S_2$: C, 42.66; H, 6.79. Found: C, 42.47; H, 6.61. ^{31}P NMR (160 MHz, $CDCl_3$): δ −18.66 (t, J = 22.3 Hz), −6.98 (d, J = 22.3 Hz). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 (t, J = 3.4 Hz, 36H, PMe_3), 1.46 (d, J = 6.8 Hz, 18H, PMe_3), 1.85 (s, 6H, CH_3), 1.94–2.02 (m, 2H, CH_2), 2.74 (t, J = 7.2 Hz, 4H, CH_2), 6.31 (s, 2H, thiophene-H), 6.51–6.53 (m, 2H, thiophene-CH=), 7.29–7.57 (m, 2H, RuCH=). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.10 (s, CH_3), 16.49 (t, J = 17.1 Hz, PMe_3), 20.13 (d, J = 21.2 Hz, PMe_3), 22.92, 38.29, 118.88, 128.38, 129.78, 134.12, 135.47, 145.22, 164.02, 202.24 (CO).

5b. Yield: 217 mg, 90%. Anal. Calcd for $C_{39}H_{68}Cl_2F_6O_2P_6Ru_2S_2$: C, 38.84; H, 5.68. Found: C, 39.12; H, 5.49. ^{31}P NMR (160 MHz, $CDCl_3$): δ −18.52 (t, J = 22.6 Hz), −6.91 (d, J = 22.6 Hz). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 (t, J = 3.8 Hz, 36H, PMe_3), 1.47 (d, J = 6.8 Hz, 18H, PMe_3), 1.81 (s, 6H, CH_3), 1.94–2.02 (m, 2H, CH_2), 2.74 (t, J = 7.2 Hz, 4H, CH_2), 6.50 (s, 2H, thiophene-H), 6.58–6.61 (m, 2H, thiophene-CH=), 7.68–7.74 (m, 2H, RuCH=). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.49 (s, CH_3), 16.54 (t, J = 14.5 Hz, PMe_3), 19.90 (d, J = 21.3 Hz, PMe_3), 116.52, 124.81, 127.58, 137.13, 147.41, 145.21, 167.94, 202.15 (CO).

General Synthesis of Complexes [RuCl(CO)(PPh_3)$_2$Py]$_2$-(CH=CH-DTE-CH=CH) (6). A mixture of complex **4** (0.20 mmol) and Py (1.0 mmol) in CH_2Cl_2 (30 mL) was stirred for 15 h. The solution was filtered through a column of Celite. The volumn of the filtrate was reduced to ca. 2 mL under vacuum. Addition of hexane (30 mL) to the residue produced a solid, which was collected by filtration, washed with hexane, and dried under vacuum.

6a. Yield: 325 mg, 88%. Anal. Calcd for $C_{103}H_{90}Cl_2N_2O_2P_4Ru_2S_2$: C, 66.91; H, 4.91. Found: C, 66.71; H, 5.08. ^{31}P NMR (160 MHz, $CDCl_3$): δ 25.53(s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.58 (s, 6H, CH_3), 1.95–2.00 (m, 2H, CH_2), 2.68 (t, J = 7.4 Hz, 4H, CH_2), 5.72–5.75 (m, 2H, thiophene-CH=), 5.95 (s, 2H, thiophene-H), 6.57 (br, 4H, pyridine-H), 7.12–7.49 (m, 62H, pyridine-H, Ph), 8.31–8.37 (m, 2H, RuCH=), 8.51 (br, 4H, pyridine-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.07 (s, CH_3), 22.32, 38.40, 123.58, 126.55, 127.21, 127.50, 128.23, 129.17, 129.80, 132.45, 133.6, 134.04, 134.76, 135.04, 144.65, 153.80, 202.96 (CO).

6b. Yield: 321 mg, 82%. Anal. Calcd for $C_{103}H_{82}Cl_2F_6N_2O_2P_4Ru_2S_2$: C, 63.28; H, 4.23. Found: C, 62.95 ; H, 4.57. ^{31}P NMR (160 MHz, $CDCl_3$): δ 26.48 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.54 (s, 6H, CH_3), 5.72–5.75 (m, 2H, thiophene-CH=), 6.08 (s, 2H, thiophene-H), 6.60 (br, 4H, pyridine-H), 7.16–7.62 (m, 62H, pyridine-H, Ph), 8.44–8.61 (br, 6H, Py-H, RuCH=). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.16 (s, CH_3), 38.40, 124.26, 134.05, 135.07, 136.61, 126.68, 127.30, 128.29, 129.30, 130.02, 132.23, 132.74, 133.43, 136.91, 146.48, 153.67, 202.89 (CO).

General Synthesis of Complexes [RuTp(CO)(PPh_3)]$_2$(CH=CH-DTE-CH=CH) (7). A mixture of complex **4** (0.20 mmol) and KTp (0.40 mmol) in CH_2Cl_2 (30 mL) was stirred for 2 h. The solution was filtered through a column of Celite to remove the KCl. The volume of the filtrate was reduced to ca. 2 mL under vacuum. Addition of hexane (30 mL) to the residue produced a solid, which was collected by filtration, washed with hexane, and dried over vacuum.

7a. Yield: 146 mg, 58%. Anal. Calcd for $C_{76}H_{74}B_2N_{12}O_2P_2Ru_2S_2$: C, 59.38; H, 4.85. Found: C, 59.61; H, 4.62. ^{31}P NMR (160 MHz, $CDCl_3$): δ 48.59 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.89 (s, 6H, CH_3), 1.90–2.00 (m, 2H, CH_2), 2.76 (t, J = 7.4 Hz, 4H, CH_2), 5.88 (m, 4H, Tp), 6.05 (s, 2H, thiophene-H),

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6.20−7.69 (m, 46H, thiophene-CH═, Ph, Tp), 7.77−7.81 (m, 2H, RuCH═). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.55 (s, CH_3), 22.87, 38.63, 105.11, 118.19, 127.93, 129.16, 129.65, 132.48, 132.91, 133.86, 134.35, 134.78, 135.07, 142.67, 143.80, 145.17, 161.13, 206.18 (CO).

7b. Yield: 179 mg, 65%. Anal. Calcd for $C_{75}H_{64}B_2F_6N_{12}O_2P_2Ru_2S_2$: C, 55.29; H, 3.96. Found: C, 55.45; H, 4.12. ^{31}P NMR (160 MHz, $CDCl_3$): δ 48.56 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.84 (s, 6H, CH_3), 5.90 (m, 4H, Tp), 6.09 (s, 2H, thiophene-H), 6.39−7.68 (m, 46H, thiophene-CH═, Ph, Tp), 7.91−7.96 (m, 2H, RuCH═). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.71 (s, CH_3), 22.65, 38.63, 105.11, 118.19, 127.93, 129.16, 129.65, 132.48, 132.91, 133.86, 134.35, 134.78, 135.07, 142.67, 143.80, 145.17, 161.13, 206.18 (CO).

General Synthesis of Complexes [RuCl(CO)(PMP)]$_2$(CH═CH-DTE-CH═CH) (8). A mixture of complex **4** (0.20 mmol) and PMP (0.40 mmol) in CH_2Cl_2 (30 mL) was stirred for 15 h. The solution was filtered through a column of Celite. The volume of the filtrate was reduced to ca. 2 mL under vacuum. Addition of hexane (30 mL) to the residue produced a solid (**8a**, brown; **8b**, green), which was collected by filtration, washed with hexane, and dried under vacuum.

8a. Yield: 217 mg, 68%. Anal. Calcd for $C_{83}H_{74}Cl_2N_2O_2P_4Ru_2S_2$: C, 62.60; H, 4.68. Found: C, 62.86; H, 4.45. ^{31}P NMR (160 MHz, $CDCl_3$): δ 48.05 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.48 (s, 6H, CH_3), 1.85−1.95 (m, 2H, CH_2), 2.49 (t, J = 7.0 Hz, 4H, CH_2), 4.20 (m, 4H, Py-CH*H*−), 4.55 (m, 4H, Py-C*H*H−), 5.24 (m, 2H, Py), 5.28 (s, 2H, thiophene-H), 6.08−6.11(m, 2H, thiophene-CH═), 7.22−7.78 (m, 44H, Ph, Py, RuCH═). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.24 (s, CH_3), 22.67, 38.35, 43.05, 118.31, 121.41, 128.20, 129.56, 130.72, 131.76, 133.63, 134.61, 138.38, 143.90, 150.75, 161.16, 207.80 (CO).

8b. Yield: 211 mg, 62%. Anal. Calcd for $C_{83}H_{68}Cl_2F_6N_2O_2P_4Ru_2S_2$: C, 58.62; H, 4.03. Found: C, 58.89; H, 4.15. ^{31}P NMR (160 MHz, $CDCl_3$): δ 47.70 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (s, 6H, CH_3), 4.20 (m, 4H, Py-CH*H*−), 4.55 (m, 4H, Py-C*H*H−), 5.20 (m, 2H, Py), 5.48 (s, 2H, thiophene-H), 6.38−6.41 (m, 2H, thiophene-CH═), 7.22−7.81 (m, 44H, Ph, Py, RuCH═). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.30 (s, CH_3), 43.00, 116.21, 121.49, 123.91, 128.22, 129.48, 130.28, 131.57, 133.65, 135.54, 138.53, 145.84, 154.90, 161.05, 207.53 (CO).

Crystallographic Details for 3a and 5b. Crystals suitable for X-ray diffraction were grown from a dichloromethane of solution **3a** and **5b** layered with hexane. A crystal with approximate dimensions of 0.20 × 0.10 × 0.10 mm^3 for **3a** and 0.30 × 0.25 × 0.20 mm^3 for **5b** was mounted on a glass fiber for diffraction experiment. Intensity data were collected on a Nonius Kappa CCD diffractometer with Mo Kα radiation (0.71073 Å) at 292 and 200 K, respectively. The structures were solved by a combination of direct methods (SHELXS-97) and Fourier difference techniques and refined by full-matrix least-squares (SHELXL-97). All non-H atoms were refined anisotropically. The hydrogen atoms were placed in the ideal positions and refined as riding atoms. Further crystal data and details of the data collection are summarized in Table 1.

Acknowledgment. The authors acknowledge financial support from National Natural Science Foundation of China (Nos. 20572029, 2072039, 20931006) and the Natural Science Foundation of Hubei Province (No. 2008CDB023).

Supporting Information Available: Absorption spectra of diarylethenes **3** and **5**−**8**, tables of bond distances and angles, and X-ray crystallographic files (CIF) for compound **3a** and **5b**. The materials are available free of charge via the Internet at http://pubs.acs.org.