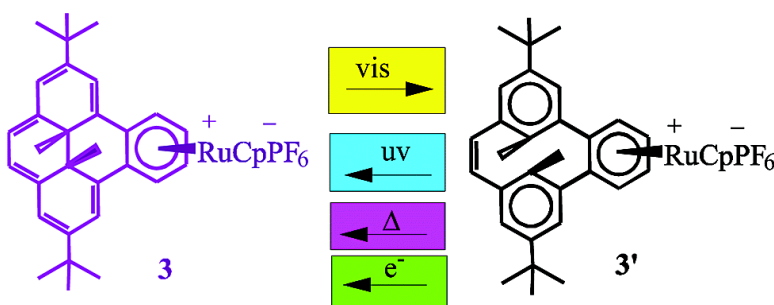


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A Photochromic, Electrochromic, Thermochemical Ru Complexed Benzannulene: an Organometallic Example of the Dimethyldihydropyrene–Metacyclophanediene Valence Isomerization

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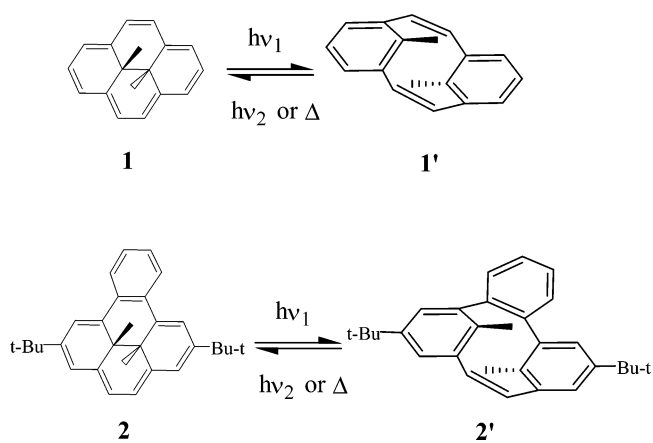
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Abstract: The preparation of the first photochromic, organometallic derivative of the diarylethene class, the CpRu-complexed benzodimethyldihydropyrene **3**, in which the organometallic is directly attached to the photochromic core, is described. The negative dark purple photochrome **3** readily bleaches to form the almost colorless cyclophanediene **3'** on irradiation with visible light. The latter switches back to **3** either photochromically with UV light, electrochromically on reduction, or thermochromically on heating. Essentially quantitative conversion between the two states is possible. The open complex **3'** thermally closes 2.6 times faster than the uncomplexed parent **2'**, but the closed form **3** opens with visible light at about 30% of the rate of uncomplexed **2**. Both open forms, complexed **3'** and uncomplexed **2'** close equally fast with UV light.

Introduction

Photochromic molecules have become a focus of intense interest recently because of potential applications to memories and switches.¹ Of the diarylethene class, the dithienylcyclopentenes of Irie² and more recently Branda and others³ are attracting much work because of their thermal bistability and fatigue resistance. Because of longer synthetic routes, another member of this class, the dimethyldihydropyrene–dimethylmetacyclophanediene photochrome **1/1'** has attracted much less attention, but it is of interest to study because it is an example of a negative photochrome where the thermally stable form (**1**) is colored.⁴ We have recently reported on several different annelated examples of **1**, which are all photochromic.⁵ The best photoswitch so far is the benzo-derivative **2/2'**.

It has an advantage over many of its dithienylcyclopentene cousins, which tend to form photostationary mixtures (e.g., 80/20 and 70/30 in refs 3a and 3b), in that it shows a clean 100%



conversion between the two photostates, **2** and **2'**. It does however, also have a disadvantage in that the Woodward–Hofmann forbidden thermal back reaction, **2'** to **2**, is not fully suppressed, $E_{\text{act}} = 25$ kcal/mol, which means that the open form **2'** has a half-life, $\tau_{1/2}$, of about one week at room temperature in solution. An alternative viewpoint is that this means that these molecules are also thermochromic!

Surprisingly to us, no organometallic derivatives of the diarylethene photochromic core of these molecules appear to be known, although examples of dithienylethenes which have metal-complexed organic species as substituents, e.g. Ru–porphyrinato attached via a pyridyl spacer,^{3b} Ru–tris-Bpy attached via an ethynyl spacer,⁶ Cu attached via a nitrile spacer,⁷

(1) Irie, M. (Guest Editor) *Chem. Rev.* **2000**, *100*, 1683–1890.

(2) Irie published 13 papers on dithienylethenes in 2002 alone. Recent examples: Kobatake, S.; Uchida, K.; Tsuchida, E.; Irie, M. *Chem. Commun.* **2002**, 2804–2805; Kobatake, S.; Morimoto, M.; Asano, Y.; Murakami, A.; Nakamura, S.; Irie, M. *Chem. Lett.* **2002**, 1224–1225; Morimoto, M.; Kobatake, S.; Irie, M. *Adv. Mater.* **2002**, *14*, 1027–1029.

(3) Recent examples: Peters, A.; McDonald, R.; Branda, N. R. *Chem. Commun.* **2002**, 2274–2275; Myles, A. J.; Branda, N. R. *Adv. Funct. Mater.* **2002**, *12*, 167–173; Mulder, A.; Jukovic, A.; Luca, L. N.; van, E. J.; Feringa, B. L.; Huskens, J.; Reinhoudt, D. N. *Chem. Commun.* **2002**, 2734–2735; Utsumi, H.; Nagahama, D.; Nakano, H.; Shirota, Y. *J. Mater. Chem.* **2002**, *12*, 2612–2619.

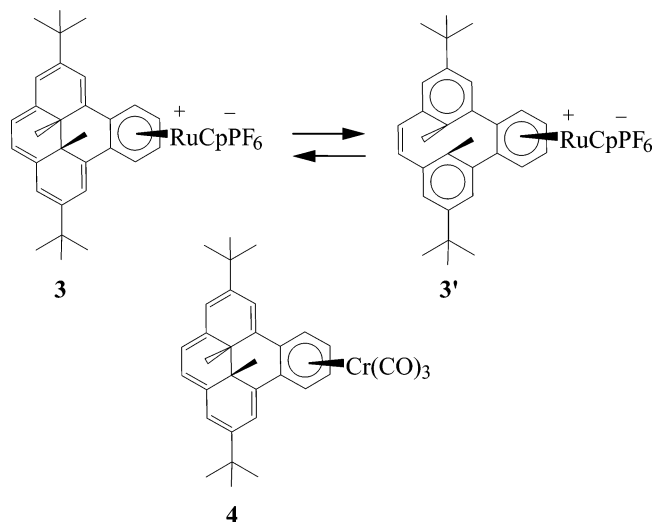
(4) Sheepwash, M. A.; Mitchell, R. H.; Bohne, C. *J. Am. Chem. Soc.* **2002**, *124*, 4693–4700; Sheepwash, M. A. L.; Ward, T. R.; Wang, Y.; Bandyopadhyay, S.; Mitchell, R. H.; Bohne, C. *Photochem. Photobiol. Sci.* **2003**, *2*, 104–112.

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(6) Fraysse, S.; Coudret, C.; Launay, J. P. *Eur. J. Inorg. Chem.* **2000**, 1581–1590.

(7) Munakat, M.; Wu, L. P.; Kuroda, S. T.; Maekawa, M.; Suenaga, Y.; Furuichi, K. *J. Am. Chem. Soc.* **1996**, *118*, 3305–3306.

or azacrown-complexed species attached through a benzyl spacer,⁸ are known. Indeed, even for other photochromic cores, organometallic derivatives are rare.⁹ Potentially however, such metal-modified switches are rather interesting, since the metal could not only modify the switching characteristics, but introduce interesting electrochemical behavior as well. This contribution reports the synthesis and properties of the organometallic CpRu–benzodimethyldihydropyrene species, photochrome 3/3'.



Results

Brun^{9a} has reported that tricarbonylchromium complexed 2H-benzochromenes are still photochromic, but the thermal ring-closing rate constant was decreased. This was just what we had hoped for our recently reported¹⁰ tricarbonylchromium derivative of **2**, namely **4**. To our surprise, we could observe no photochromic reaction of **4** at all. The compound did not even decompose! We were unsure whether this was unique to the chromium compound, or whether any organometallic derivative of **2** would shut down the photochemistry. We thus decided to investigate the synthesis of the ruthenium compound **3**.

Synthesis. RuCp complexes of naphthalene and pyrene have been prepared¹¹ using tris(acetonitrile)cyclopentadienylruthenium (I) hexafluorophosphate.¹² Indeed, reflux of the latter with benzodihydropyrene **2** in dichloroethane for 19 h, followed by chromatography, gave 69% of dark purple plum-colored **3**, mp 176–178 °C. The crystals gave a correct LSIMS HRMS (found: 561.211; calcd for C₃₅H₃₉¹⁰²Ru: 561.210) and correct elemental analysis. The ¹H NMR spectrum confirmed that the annulene **2** had been complexed, since the internal methyl protons appeared (acetone-*d*₆) at δ –0.77 and –0.31, less shielded than those (δ –1.59) of the uncomplexed **2**, consistent with the reduction in ring current in the annulene ring on complexation.^{10,13} As expected, the Cp protons appeared as a

Table 1. Rate Constants (min⁻¹) for the Thermal Closing Reaction 3' to 3

temp (K)	rate (min ⁻¹) ^a
313	0.0026(5)
330	0.0154(9)
339	0.0468(70)

^a Values in parentheses are 3σ errors, based on integration error estimates.

singlet at δ 5.21. Full proton and carbon assignments are given in the Experimental Section.

Photochemistry. On irradiation of a deep purple acetone solution of complex **3** with visible light (household tungsten–halogen lamp, 500 W), the sample bleached to very pale violet, forming the cyclophanedienene complex **3'**. The latter had internal methyl protons at δ 1.10 and 1.46 consistent for a metacyclophane, and showed essentially a benzenoid UV spectrum with tail. This opening process could be conveniently followed by ¹H NMR in acetone-*d*₆. Irradiation of **3** at the same time and side by side to an equimolar solution of **2**, allowed a comparison of the relative rates of ring-opening of **3** relative to the parent **2**. The relative amounts of 3/3' and 2/2' could easily be estimated by integration of their proton signals (see Experimental Section), from which apparent relative rate constants could be determined. The complex **3** was found to photo-open at 30% of the rate of the benzo parent **2**. Thus, under the same conditions, those of ample light flux, complexation has slowed the photo-opening rate by some three times.

Photoclosing of 3' to **3**, occurred very quickly with UV light. Again, using samples with the same initial concentration, under identical irradiation conditions, led to a photoclosing rate that had no noticeable difference between 3' and 2'. This is consistent with our previous studies, in which the quantum yields of the closing reaction are considerably higher than the opening reaction and are not much affected by changes to the molecule.⁴

Thus, CpRu-complexation of **2** has led to the photoswitchable 3/3', which can be easily switched quantitatively between the two photoisomers.

Thermochemistry. The thermal closing reaction of 3' to **3** was conveniently followed by ¹H NMR in CD₃CN. Integration of the Cp signals at δ 5.35 for 3' and 5.02 for **3** was most convenient to obtain the rate constants (see Experimental Section) at 313, 330, and 339 K, Table 1.

An Arrhenius plot gave *E*_{act} = 23.0(4) kcal/mol, and an Eyring plot gave Δ*H*[‡] = 22.4(4) kcal/mol and Δ*S*[‡] = 7.1(1.1) cal mol⁻¹ K⁻¹. We have adopted τ_{1/2} at 46 °C (319 K) as the most convenient way to compare different thermochromes.⁵ The value for the parent 2' to **2** is 5.75 h, while that for the complex 3' to **3** is 2.2 h. Complexation has thus increased the thermal closing rate by 2.6 times. Nevertheless, at room temperature (293 K), the thermal return reaction is still slow, *t*_{1/2} = 55 h, making complex 3/3' an acceptable switch.

Electrochemistry. We recently⁵ have shown that electrochemical readout of the state of the 2/2' switch is possible. The 18π dihydropyrene **2** is easy to oxidize electrochemically and shows a peak anodic current (*E*_{p,a}) centered at 0.75 V (Ag⁰ reference electrode). In contrast, the benzenoid cyclophanedienene 2' was redox silent over the same 0–1.00 V potential window.

The electrochemical behavior of ruthenium complex **3** was investigated in *N,N*-dimethylformamide (DMF) with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as sup-

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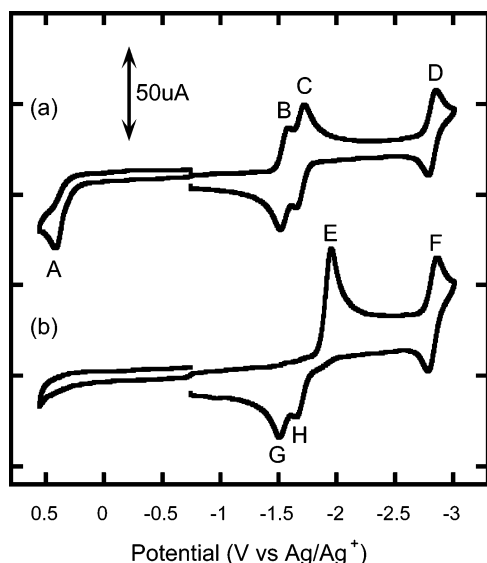


Figure 1. Cyclic voltammograms of **3** in 0.1 M TBAPF₆/DMF at 0.2 V s⁻¹ scan rate. (a) CV before visible light irradiation; (b) CV after visible light irradiation.

Table 2. Electrochemical Data (Potentials, V vs Ag/Ag⁺) for Complex **3** in 0.1 M TBAPF₆/DMF

(A) Before Irradiation with Visible Light ^a			
$E^{\circ}_{(A)}$	$E^{\circ}_{(B)}$	$E^{\circ}_{(C)}$	$E^{\circ}_{(D)}$
0.381	-1.551	-1.688	-2.819
(B) After Irradiation with Visible Light ^a			
$E_{p(E)}$ ^b	$E^{\circ}_{(F)}$		
-1.944	-2.820		

^a Letters in parentheses refer to the labels in Figure 1a,b. ^b Peak potential at 0.2 V s⁻¹.

porting electrolyte, using cyclic voltammetry (CV). Figure 1 shows a typical CV with electrochemical data summarized in Table 2.

Complex **3** exhibits two reversible one-electron reductions (B and C in Figure 1a) corresponding to addition of one and then a second electron, respectively. A further one electron reversible reduction is observed at more negative potentials (D in Figure 1a). These reversible reductions allowed for the calculation of standard reduction potentials listed in Table 2. It should be noted that the parent **2** only adds one electron reversibly at -1.30 V, presumably to give radical anion, and a second electron irreversibly at about -2.1 V, which would form the strongly antiaromatic dianion. Complex **3** exhibits a one-electron oxidation process (A) that is irreversible at scan rates up to 1 V s⁻¹. At faster scan rates (i.e. >1 V s⁻¹) the oxidation became reversible and allowed for the determination of a standard oxidation potential (0.38 V), considerably lower than that of parent **2** (0.75 V).⁵

The dihydropyrene form **3** was converted to the cyclophane form **3'** by irradiating the entire electrochemical cell with visible light from a tungsten lamp. This caused the deep purple solution to change to a pale violet color. The CV after irradiation (Figure 1b) shows the disappearance of the reduction waves B and C (Figure 1a) and the appearance of a new irreversible two-electron reduction (E in Figure 1b). This wave did not become reversible up to 100 V s⁻¹. At more negative potentials, a further one-electron reversible reduction (F in Figure 1b) is observed that

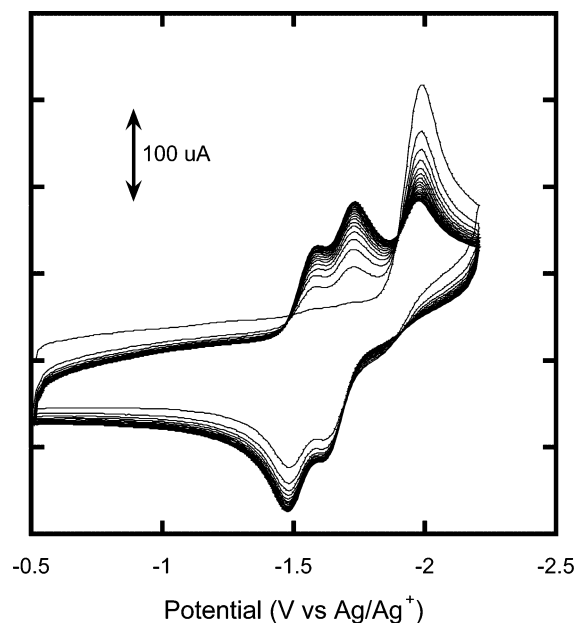
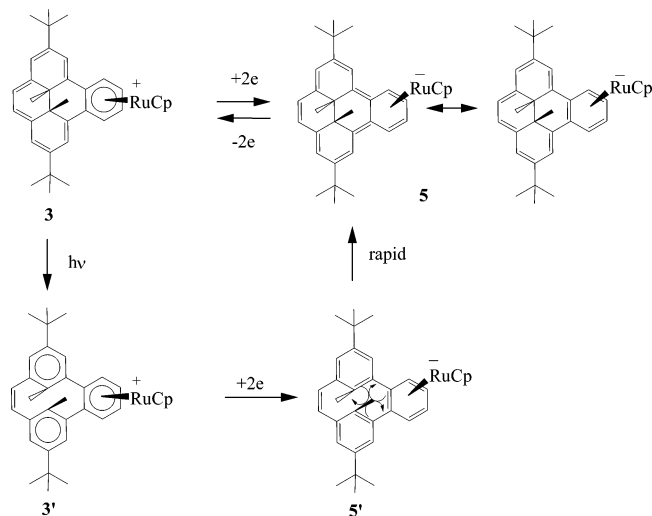


Figure 2. Cyclic voltammogram of complex **3** in 0.1 M TBAPF₆/DMF at 5 V s⁻¹ scan rate when the potential is repeatedly cycled between -0.5 and -2.2 V.

has an identical standard reduction potential as that before irradiation. Irradiation also resulted in the disappearance of the oxidation process, within the voltage range used, as was observed for parent **2'**.⁵

Also present in the CV after visible irradiation are two anodic waves (G and H in Figure 1b) that occur only when the potential is scanned through the irreversible reduction. These waves occur at the same potentials as the anodic portion of the waves B and C in the CV of the closed molecule. Reversing the potential after the appearance of these anionic waves, and scanning to more negative potentials once again, results in the appearance of two new cathodic waves that have identical peak potentials as the two waves in the closed form. A decrease in the peak current of the irreversible wave is also observed. Repeated cycling (Figure 2) of the potential between -0.5 and -2.2 V resulted in the continuous decrease of the peak current for the irreversible wave with a concomitant increase in the peak currents for the two new waves that appear at more positive potentials. These peaks allowed for the determination of their standard reduction potentials which were found to be identical to those before irradiation with visible light. This suggests that upon reduction, the open cyclophane form **3'** converts back to the closed dihydropyrene form, with the latter being responsible for the anodic peaks (G and H in Figure 1b) as the dianion and radical anion are oxidized back to the neutral form of closed **3**. After repeated cycling experiments the deep purple color of the original solution returned. This could be converted back to the pale violet color by irradiation with visible light, further confirming the presence of the closed form **3** that results from electrochemical processes. This switching behavior accounts for the similarities observed in the CVs of the open (**3'**) and closed (**3**) forms. Upon sweeping through the potential where the open form is reduced, **3'** converts to its closed form, and the CV, from that point on, appears identical to that recorded for the closed form, resulting in the identical standard reduction potentials observed for waves D and F. Therefore, ruthenium complex **3** is exhibiting electrochemical as well as a photo-

chemical switching behavior. To some extent, the electrochemical switching can be understood in terms of resonance structures:



In the nonreduced forms **3** and **3'**, the Ru(II) is probably bound η^6 . On reduction of the open form **3'** to **5'**, the addition of two electrons could reduce the ruthenium to Ru(0), which for an 18e count would mean η^4 bonding, leaving the fused bridge alkene electrons more available to undergo the electrocyclic rearrangement to form the closed reduced species **5** (note: the parent **1'** undergoes more rapid thermal closing than the benzo form **2'**, in which the fused bridge electrons are delocalized in the benzene ring). The resonance structures of closed **3** and **5** resemble those of naphthalene, and indeed in such complexes, Ru could¹⁵ show variable haptotropic behavior, either η^4 or η^6 . Removal of 2e from **5** then returns closed **3**.

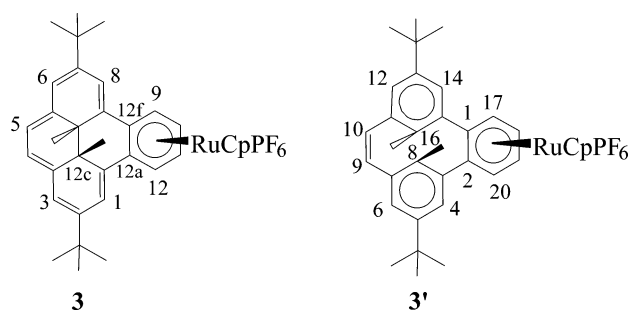
Conclusions

Ruthenium complex **3** is the first example of an organometallic derivative of the photochromic core of the diarylethene class photochromes. It is a negative photochrome, where the thermally stable form is colored (deep purple). Under identical conditions, it photo-opens (bleaches) at 30% of the rate of the uncomplexed parent **2**, but photocloses at a similar rate. Essentially quantitative conversion between the closed and open states is possible. At room temperature, 20 °C, the thermal return reaction, is acceptably slow, $t_{1/2} = 55$ h. At higher temperatures, the open molecule, **3'**, is a reasonable thermochrome ($t_{1/2}$ at 46 °C = 2.2 h) and closes at a rate 2.6 times faster than the uncomplexed **2'**. The molecule is also electrochromic. Electrochemical reduction of the open form **3'** converts it to the closed form **3**. Thus, the ring-opening reaction only proceeds photochemically, but the ring-closing reaction can be achieved photochemically, thermally, or electrochemically. As of February, 2003, we know of no other example.

Experimental Section

Melting points were determined on a Reichert 7905 melting point apparatus integrated to an Omega Engineering model 199 Chromel—

alumel thermocouple. UV–visible spectra were recorded on a Cary 5 UV–vis–NIR spectrometer. Proton NMR spectra were recorded on a Bruker AMX 360 spectrometer at 360 MHz in $(\text{CD}_3)_2\text{CO}$, using the acetone peak at 2.04 ppm for calibration. Kinetic data were obtained using a Bruker AC 300 MHz spectrometer. Carbon NMR spectra were recorded at 90.6 MHz, using the acetone peak at 29.8 ppm for calibration. Where peaks within the same sample are very close in chemical shift, a third decimal place is given. Exact mass measurements were done on a Kratos Concept-H instrument using perfluorokerosene as the standard. Elemental analyses were performed by Canadian Microanalytical Services Ltd., Vancouver, BC. All evaporations were carried out under reduced pressure on a rotary evaporator, or by using an oil pump and dry ice condenser. SiGel refers to Merck silica gel, 60–200 mesh. Radial chromatography was performed on a Harrison Research Chromatotron, using glass plates coated with Merck TLC grade 7749 silica gel. Solvents were deoxygenated by bubbling argon through for 5–10 min. NMR assignments were made on the basis of 2D COSY/NOESY experiments for ^1H and HETCORR/HMOCB experiments for ^{13}C . H-1,2 means H-1 and H-2; H-1/2 means H-1 or H-2. Expanded data sets were used to obtain coupling constant data. To make the NMR assignments clear, numbering of the relevant parent structure is shown here.



[η^5]-Cyclopentadienylruthenium(I)-[9,10,11,12,12a,12f- η^6]-2,7-ditert-butyl-trans-12c,12d-dimethyl-12c,12d-dihydropyrene Hexafluorophosphate (3**). Benzodihydropyrene **2'**¹⁴ (100 mg, 0.26 mmol) and $[\text{CpRu}(\text{CH}_3\text{CN})_3]\text{PF}_6$ ¹² (187 mg, 0.40 mmol) in 1,2-dichloroethane (15 mL) were degassed by three freeze–pump–thaw cycles and then were heated to 80 °C for 19 h with stirring, under argon. The solvent was removed in vacuo, and the solid was purified by radial chromatography (2-mm plate). The complex **3** was eluted with dichloromethane–ethyl acetate (9:1) and gave 130 mg (69%) of dark purple–plum crystals from acetone–hexane, mp 176–178 °C. ^1H NMR δ 8.32 (dd, $J = 1.35$, 0.28 Hz, H-8), 8.29 (dd, $J = 1.35$, 0.34 Hz, H-1), 8.01–7.97 (m, H-12), 7.93–7.89 (m, H-9), 7.23 (dd, $J = 1.30$, 0.54 Hz, H-3), 7.18 (dd, $J = 1.34$, 0.54 Hz, H-6), 6.92 (dd, $J = 6.33$, 0.60 Hz, H-5), 6.91 (dd, $J = 6.33$, 0.60 Hz, H-4), 6.54–6.48 (m, H-11,10), 5.21 (s, 5, Cp-H), 1.41 (s, 18, *t*-Bu-H), –0.31 (s, 3, 12c-CH₃), –0.77 (s, 3, 12d-CH₃) (for assignment method, see ref 10; J values ± 0.05 Hz); ^{13}C NMR δ 145.68 and 145.61 (C-2,7), 140.18 and 139.82 (C-3a,5a), 132.30 and 131.49 (C-12b,12e), 125.51 (C-1), 125.12 (C-8), 123.99 and 123.85 (C-4,5), 123.77 (C-3), 123.39 (C-6), 97.47 (C-12a), 95.73 (C-12f), 85.00 and 84.97 (C-10,11), 82.40 (C-9), 81.79 (Cp), 79.76 (C-12), 38.25 (C-12d), 37.78 (C-12c), 35.85 and 35.81 (C(CH₃)₃), 30.16 (–C(CH₃)₃), 23.29 (12c-CH₃), 18.91 (12d-CH₃). UV (acetonitrile) λ_{max} nm 242 (28 800), 317 (24 300), 381 (19 200), 547 (4700). IR (KBr) ν 3114(w), 2956(m), 2918(m), 2868(m), 1462(w), 1440(w), 1415(w), 1365(w), 1334(w), 1261(w), 1233(w), 839(vs), 557(s) cm^{-1} . LSIMS MS m/z 561.2 (M^+). HRMS calcd for $\text{C}_{35}\text{H}_{39}^{102}\text{Ru}$, 561.2089; for $\text{C}_{35}\text{H}_{40}^{101}\text{Ru}$, 561.2186. Found, 561.2107. Anal. Calcd for $\text{C}_{35}\text{H}_{40}\text{RuPF}_6$: C, 59.57; H, 5.57. Found: C, 60.01; H, 5.55.**

Photoisomer 3'. The Ru complex **3** (18 mg) in d_6 -acetone (0.65 mL) in an NMR tube cooled by an electric fan was irradiated with a 500-W household tungsten–halogen lamp (Globe Electric (Montreal, Quebec, Canada), T-3, 8500 lumens) until the color of the solution

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was pale violet and the NMR spectrum showed no high-field protons around $\delta -1$ (about 20 min).

The solution then contains essentially pure cyclophane form **3'**, ^1H NMR (300 MHz) δ 7.30 (d, $J = 1.6$ Hz, H-4/14), 7.25 (d, $J = 2.4$ Hz, H-14/4), 7.07 (d, $J = 1.6$ Hz, H-6/12), 7.05 (d, $J = 2.4$ Hz, H-12/6), 7.03 (d, $J = 5.6$ Hz, H-20/17), 6.86 (d, $J = 5.6$ Hz, H-17/20), 6.60 (t, $J = 5.6$ Hz, H-19/18), 6.59 (s, 2, H-9,10), 6.44 (t, $J = 5.6$ Hz, H-18/19), 5.58 (s, 5, Cp), 1.35 and 1.29 (s, 9 each, 5,13-*t*-Bu), 1.46 and 1.10 (s, 3 each, 8,16-Me). ^{13}C NMR (d_6 -acetone, 75.5 MHz) δ 152.22, 151.21, 140.75, 140.60, 138.86, 138.00, 133.85, 133.17, 132.87, 131.69, 129.59, 125.91, 125.77, 110.81, 110.11, 89.53, 86.63, 85.52, 85.33, 83.27(Cp), 35.06, 34.94, 31.66(*t*-Bu), 31.48(*t*-Bu), 19.71(Me), 18.90-(Me). UV (acetonitrile) λ_{max} nm (ϵ_{max}) 200 (58 000), 212 (50 000), 243 (43 000).

Relative Photo-Opening Rate Studies. This was carried out exactly as the experiment to generate photoisomer **3'** above, except that an equimolar solution of the parent benzodihydropyrene **2** (10 mg in 0.65 mL of d_6 -acetone) was irradiated at the same time, side by side. Every 30 s, the sample was removed, its ^1H NMR spectrum was recorded, and then irradiation was continued for a further 30 s. The ratios of the open and closed forms, **3'** and **3**, were determined at each time interval from the integrations of the Cp protons at δ 5.58 and 5.21, respectively. For the benzopyrene **2**, the internal methyl protons at $\delta -1.59$ were used, and for cyclophane **2'**, those at $\delta 1.27$. The apparent relative rate constants were obtained using the equation: $\ln(c_o/c_i) = kt$ where c_o is the mole fraction of the closed form at the beginning of the experiment (1 in this case), and c_i is the mole fraction of the closed form at each time = closed/closed + open. The plot of $\ln(c_o/c_i)$ vs t (min) was linear (available in Supporting Information), and yielded rate constants of 0.285 min^{-1} for **2** and 0.0837 for **3**.

Relative Photoclosing Rate Studies. Approximately equimolar (5×10^{-5}) solutions of **2'** and **3'** in toluene were generated as in the photo-opening experiment above. The visible absorptions of the closed forms at 505 nm (**2**) and 548 nm (**3**) were then monitored at intervals by UV-vis spectroscopy as the samples were irradiated side by side using the same pencil low pressure Hg(Ar) UV lamp (Oriel 6035). A plot of concentration of the closed form vs time was essentially linear (available in Supporting Information) and both had the same slope, indicating that the rates of closing were almost identical.

The Thermal Closing Studies. The thermal closing of **3'** to **3** was followed using ^1H NMR at three temperatures. The complex **3** (20 mmol) in CD_3CN (0.65 mL) was bleached as in the photo-opening experiment above. The solution of cyclophane **3'** was then held at the

experiment temperature (40, 57, and 66 °C respectively) for the desired time interval, was immersed in ice-water to stop the thermal reaction, and then its ^1H NMR spectrum was taken as quickly as possible to measure the ratio of open and closed forms by means of the Cp proton integrals at 5.35 (**3'**) and 5.02 (**3**). The rate constants were then obtained by plotting $\ln(c_o/c_i)$ vs time, as described above for the visible opening experiment, except that now c_o is the mole fraction of the open form at the beginning of the experiment, and c_i is the mole fraction of the open form at time interval i . The rate plots are available in the Supporting Information. The rate constants that were determined are given in Table 1, above. Arrhenius and Eyring plots (Supporting Information) then generated the thermodynamic data in the text above.

Electrochemistry: Cyclic Voltammetry. Experiments were performed using a Bioanalytical Systems (BAS) CV50W voltammetric analyzer interfaced to a personal computer. BAS software was used to conduct the experiments as well as analyze the derived data. Measurements were conducted in a glass cell at room temperature. All glassware was dried in an oven before use and assembled, hot while flushing with argon. The working electrode was glassy carbon (BAS) and the counter electrode was a platinum wire. The reference electrode was a silver wire housed in a glass tube sealed with a porous Vycor tip and filled with a 0.1 M solution of AgNO_3 in acetonitrile. Acetonitrile was distilled from calcium hydride prior to use. All potentials were referenced versus Ag/AgNO_3 . *N,N*-Dimethylformamide (DMF) was distilled under reduced pressure over calcium hydride prior to use. Tetrabutylammonium hexafluorophosphate (TBAPF_6) (Aldrich) was recrystallized three times from 95% ethanol and dried under vacuum at 60 °C prior to use and stored in a desiccator. Ferrocene was recrystallized from pentane and sublimed once before use. Concentrations of ~ 2 mM of ruthenium complex **3** in 0.1 M TBAPF_6 in DMF were used. Positive feedback IR compensation was used in all experiments to minimize the effects of uncompensated solution resistance.

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Supporting Information Available: Rate plots, Arrhenius and Eyring plots (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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