

Photodimerization of (η^5 -Cyclopentadienyl)(η^6 -dibenzo-*p*-quinodimethane)ruthenium(II) Hexafluorophosphate

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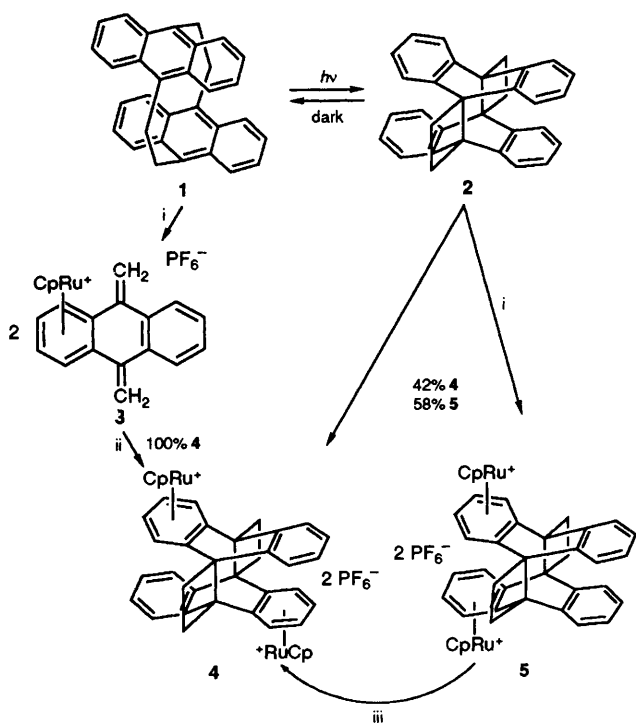
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Photodimerization of $[(\text{RuCp})(\eta^6\text{-dbqm})]^+\text{PF}_6^-$ **3** (Cp = η^5 -cyclopentadienyl; dbqm = dibenzo-*p*-quinodimethane) in solution using visible light selectively afforded a stable organometallic adduct of the normally labile intramolecular photoisomer of [2.2](9,10)anthracenophane.

[2.2](9,10)Anthracenophane **1** exists in two orange crystalline phases (the α and β forms) which form a colourless intramolecular [4 + 4] photoisomer **2** on irradiation with visible light in solution or in the solid state (Scheme 1).¹ The unstable photoisomer **2** reverts to **1** exothermically in the dark.^{1,2} The reversible intramolecular photoaddition in **1** has been exten-

sively studied since its photoreaction stores a significant fraction of photon energy as chemical potential energy,³⁻⁵ but the back reaction is too slow to be of practical use. We were interested in using organoruthenium cations to coordinate one or more of the benzo rings of **1**, sterically hindering the photoaddition reaction and facilitating the back reaction. Higher storage enthalpies, enhanced absorption at long wavelengths and higher quantum yield for the photodimerization were also potential benefits from such coordination. However, treatment of **1** with 2 equiv. of $[\text{RuCp}(\text{MeCN})_3]^+\text{PF}_6^-$ resulted in cleavage of the ethano bridges to form the organoruthenium dibenzo-*p*-quinodimethane (dbqm) complex $[(\text{RuCp})(\eta^6\text{-dbqm})]^+\text{PF}_6^-$ **3**, in which the highly reactive dibenzo-*p*-quinodimethane moiety is stabilized by η^6 -coordination with the CpRu^+ group (Scheme 1).^{6,7}

On crystallization of the dbqm complex **3** from nitromethane by diethyl ether diffusion under ambient visible light conditions, we obtained crystals of a dimerized product, *exo-anti*- $[(\text{RuCp})_2(\eta^6:\eta^6\text{-2})]^{2+} 2[\text{PF}_6]^-$ **4** (Scheme 1). Complex **4** is an air-stable white crystalline solid and was characterized using ¹H NMR, mass spectroscopy (MS) and elemental analysis.† Mass spectrometry [fast atom bombardment (FAB)] showed peaks at *m/z* 886 (*M* - 145, - PF_6^-) and 741 (*M* - 290, - 2PF_6^-), consistent with a dimeric product. The



Scheme 1 Reagents and conditions: i, $[\text{RuCp}(\text{MeCN})_3]^+\text{PF}_6^-$, thf, room temp.; ii, MeNO_2 , 5 days, visible light; iii, MeNO_2 , several days

† Selected physical data for **4**: m.p. >242 °C, decomp., satisfactory C and H analyses were obtained. FAB-MS, *m/z* 886 (7), 741 (6), 575 (5), 374 (100%). ¹H NMR (300 MHz, CD_3NO_2): δ 7.52 (4H, dd, *J* 3.3 and 5.6 Hz, arene), 7.34 (4H, dd, *J* 3.3 and 5.6 Hz, arene), 6.39 (4H, dd, *J* 3.3 and 5.6 Hz, coordinated arene), 5.96 (4H, dd, *J* 2.4 and 4.5 Hz, coordinated arene), 4.59 (10H, s, Cp), 3.65 (4H, m, 2 CH_2), 2.97 (4H, m, 2 CH_2). For **5**: since this complex converts to **4** in solution, we have been unable to isolate and purify it. ¹H NMR (in CD_3NO_2): δ 7.41 (4H, dd, *J* 3.3 and 5.6 Hz, arene), 7.19 (4H, dd, *J* 3.3 and 5.6 Hz, arene), 6.55 (4H, dd, *J* 3.3 and 5.6 Hz, coordinated arene), 6.06 (4H, dd, *J* 2.4 and 4.5 Hz, coordinated arene), 4.48 (10H, s, Cp), 3.30–3.00 (8H, m, 4 CH_2).

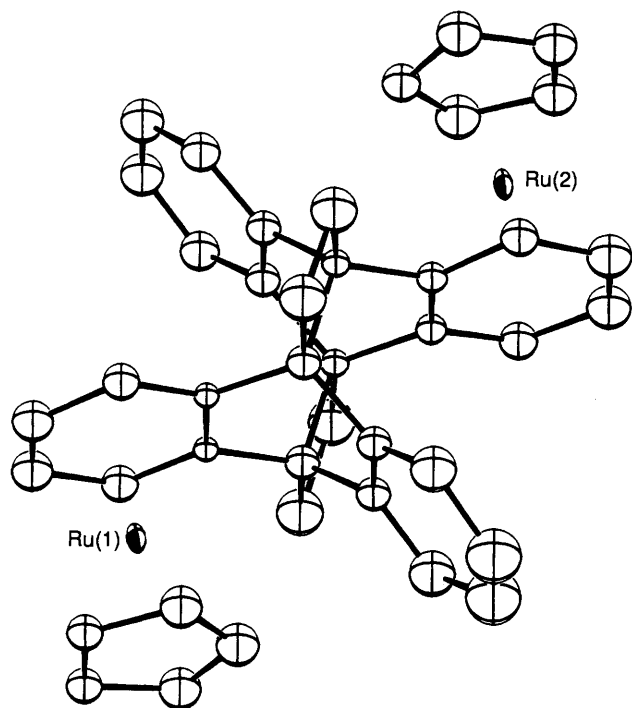


Fig. 1 ORTEP drawing of preliminary crystal structure of **4**

protons on the ethano bridges in **4** appear as multiplets at δ 3.65 and 2.97 (CD_3NO_2), compared to the corresponding protons in complex **3** [$(\text{CD}_3)_2\text{CO}$, δ 6.23 (s) and δ 6.19 (s)],⁶ cyclophane **1** [CDCl_3 , δ 4.18 (s)] and photoisomer **2** [CDCl_3 , δ 2.95 (s)]. The structure of **4** has been confirmed by a preliminary X-ray crystallographic study as shown in Fig. 1. ‡

Since the photoisomer complex **4** was obtained during recrystallization and gave a single isomer, we considered the possibility that dbqm complex **3** crystallized prior to photodimerization in the solid state, the product of which would be controlled by the packing arrangement in the crystals. However, photolysis of crystals of **3** did not give any reaction. In solution, dimerization of **3** in nitromethane did not occur in the dark, even under refluxing conditions. We repeated the photodimerization of **3** in an NMR tube (CD_3NO_2) under ambient light conditions to confirm photodimerization in solution and to observe if any of the *exo-syn*- $[(\text{RuCp})_2(\eta^6:\eta^6\text{-}2)]^{2+} 2[\text{PF}_6]^-$ **5** isomer was produced. ^1H NMR spectra recorded periodically over 15 days indicated that only *exo-anti* isomer **4** was formed. It would seem likely that photodimerization of **3** is the result of two isolated [2 + 2] cycloadditions, possibly directed by secondary orbital interactions to give dimer instead of polymer. However, [4 + 4] cycloaddition, followed by fast closure of the resulting primary bridge radicals is possible, as is an undefined reaction type controlled by perturbation of the molecular orbitals of the dbqm moiety by coordination to the ruthenium. It is clear that to dimerize, two molecules of **3** must approach each other in a cofacial fashion with the CpRu^+ groups pointing outward. The stereospecific dimerization may result from differential attraction between the benzo rings complexed with an electron-withdrawing CpRu^+ group⁸ and the more electron rich non-complexed benzo rings, reducing face-to-face π -electron repulsion.

‡ Space group: *Pnma*, $Z = 4$, $a = 23.409(9)$, $b = 18.533(7)$, $c = 9.442(4)$ Å, $V = 4091.5(6)$ Å³. The present *R*-factor is 0.104. Refinement is still in progress; full details will be published later.

Photolysis of a nitromethane solution of $[(\eta^5\text{-C}_5\text{Me}_5\text{Ru})(\eta^6\text{-dbqm})]^+(\text{SO}_3\text{CF}_3)^{-7}$ under the same conditions gave no detectable dimerization. This is likely due to steric interactions between the methyl groups of the $\eta^5\text{-C}_5\text{Me}_5$ ring and the opposing non-coordinated benzo ring if the $\eta^5\text{-C}_5\text{Me}_5$ analogue of **4** were to form but may be due to weaker electronic effects from $\eta^5\text{-C}_5\text{Me}_5\text{Ru}^+$ relative to the CpRu^+ group.⁸ Further studies of the generality and synthetic application of the selective photodimerization demonstrated here may have broader implications in synthetic methodology and in understanding the photochemistry of organometallic compounds.

In contrast to photodimerization giving *exo-trans* isomer **4** selectively, reacting photoisomer **2** directly with 2 equiv. of $[\text{RuCpMeCN}]_3^+ \text{PF}_6^-$ in tetrahydrofuran at room temperature for 1 h, followed by workup of the resulting solution, gave both geometric isomers **4** and **5** in the ratio of 42 : 58 by ^1H NMR, as depicted in Scheme 1. However, conversion of *exo-syn* isomer **5** to *exo-anti* isomer **4** in solution slowly occurs over 15 days at room temperature (CD_3NO_2 , by ^1H NMR). Precipitation with diethyl ether gave nearly pure *exo-anti* isomer **4**. This kind of ring-shift isomerization reaction is related to that observed in monocyclopentadienylruthenium(II) complexes of rubrene⁹ and suggests that **4** is the more thermodynamically stable isomer. Kinetic measurements and investigations of the mechanism of this ring shift isomerization are in progress.

In spite of our expectation to the contrary, and in contrast to photoisomer **2**, complex **4** is quite stable in the solid state and in solution, even after heating to reflux in the dark for 3 days or exposing to visible light for more than 10 days (by ^1H NMR). It has been postulated that the instability of **2**, other anthracene photodimers, lepidopterenes and dianthronyl compounds arises from weakening of the bridging bonds due to overlap of the p-orbitals of the benzo rings with the σ -antibonding orbitals of the bridging bonds.⁵ Localization of electron density in the p-orbitals of the benzo rings in **4** by coordination to the ruthenium would counteract this effect and stabilize the bridging bonds. Experiments to investigate analogous bond stabilization in other anthracene photodimers and related compounds by complexation with CpRu^+ groups are ongoing.

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