

Photochemical [2+2] cycloaddition of the olefinic double bonds in the supramolecular rectangle $[\text{Ru}_4(\eta^6\text{-}p\text{-cymene})_4(\mu\text{-oxalato})_2(\mu\text{-4,4'}$ -bipyridylethylene) $)]^{4+}$

Nicolas P.E. Barry, Bruno Therrien*

Institut de Chimie, Université de Neuchâtel, Case postale 158, CH-2009 Neuchâtel, Switzerland

ABSTRACT

Self-assembly of 4,4'-bipyridylethylene (bpe) bidentate connector with the dinuclear arene ruthenium clip $[\text{Ru}_2(\eta^6\text{-}p\text{-cymene})_2(\mu\text{-oxalato})\text{Cl}_2]$ in the presence of silver triflate affords the cationic organometallic rectangle $[\text{Ru}_4(\eta^6\text{-}p\text{-cymene})_4(\mu\text{-oxalato})_2(\mu\text{-bpe})_2]^{4+}$ ($[\mathbf{1}][\text{CF}_3\text{SO}_3]_4$). Upon UV irradiation of a methanol solution of $[\mathbf{1}]^{4+}$, dimerisation of the olefinic double bonds of the two parallel bpe ligands occurs, thus giving rise to the [2+2] cycloaddition derivative $[\text{Ru}_4(\eta^6\text{-}p\text{-cymene})_4(\mu\text{-oxalato})_2(\mu\text{-tpcb})]^{4+}$ ($[\mathbf{2}][\text{CF}_3\text{SO}_3]_4$) (tpcb = tetrakis(4-pyridyl)cyclobutane). The [2+2] photodimerisation reaction was followed by ^1H NMR spectroscopy. Moreover, the molecular structure of these two systems was deduced by one-dimensional and two-dimensional NMR experiments (^1H , ^{13}C , ROESY, COSY, HSQC). These data suggest the formation of only the *rctt*-tetrakis(4-pyridyl)cyclobutane isomer.

Keywords:

Bridging ligands, Arene ligands, Ruthenium, Supramolecular chemistry, [2+2] Cycloaddition

In recent years, template-controlled reactivity of olefins by supramolecular assemblies for photochemical [2+2] dimerisation has been widely used in view to obtain new materials [1]. Among the different building blocks available to generate supramolecular assemblies, half-sandwich complexes are becoming more and more popular in supramolecular chemistry. They have been exploited to build up rectangles, macrocycles and cages [2–10]. Last year, Jin's group has synthesised two organometallic rectangles of the general formula $[\text{M}_4(\eta^5\text{-Cp}^*)_4(\mu\text{-oxalato})_2(\mu\text{-bpe})_2]^{4+}$ (bpe = 4,4'-bipyridylethylene; Cp^* = pentamethylcyclopentadienyl) incorporating half-sandwich complexes of Rh(III) and Ir(III) connected by oxalato and bpe ligands. In the solid state, upon UV irradiation of a crystal, the two olefinic double bonds which are positioned parallel to each other undergo intramolecular photochemical [2+2] cycloaddition, thus giving rise to the corresponding cyclobutane derivatives $[\text{M}_4(\eta^5\text{-Cp}^*)_4(\mu\text{-oxalato})_2(\mu\text{-tpcb})]^{4+}$ (tpcb = tetrakis(4-pyridyl)cyclobutane), see Fig. 1 [11].

Recently we used arene ruthenium complexes as building blocks to generate a series of discrete cationic supramolecular assemblies [12]. Herein we report the synthesis and characterisation of a tetranuclear cation incorporating *p*-cymene ruthenium building blocks, bridged by oxalato ligands, and connected by 4,4'-bipyridylethylene bidentate connectors. In solution, the two olefinic double bonds react under UV irradiation to afford the intramolecular [2+2] cycloaddition adduct.

Addition of AgCF_3SO_3 to the dinuclear complex $[\text{Ru}_2(\eta^6\text{-}p\text{-cymene})_2(\mu\text{-oxalato})\text{Cl}_2]$ [3a] in the presence of 4,4'-bipyridylethylene (bpe) leads to the formation of the tetranuclear cation $[\text{Ru}_4(\eta^6\text{-}p\text{-cymene})_4(\mu\text{-oxalato})_2(\mu\text{-bpe})_2]^{4+}$ ($[\mathbf{1}]^{4+}$) in good yield ($\approx 80\%$), see Scheme 1. This rectangular cation is isolated as its triflate salt $[\mathbf{1}][\text{CF}_3\text{SO}_3]_4$ [13].

When a CH_3OH solution of $[\mathbf{1}][\text{CF}_3\text{SO}_3]_4$ is irradiated for a period of 60 h using a Hg lamp (180 W), a photochemical [2+2] cycloaddition reaction takes place, thus giving rise in excellent yield to the cationic cyclobutane derivative $[\text{Ru}_4(\eta^6\text{-}p\text{-cymene})_4(\mu\text{-oxalato})_2(\mu\text{-tpcb})]^{4+}$ ($[\mathbf{2}]^{4+}$) (tpcb = tetrakis(4-pyridyl)cyclobutane), see Scheme 2. The rectangular cation $[\mathbf{2}]^{4+}$ is isolated and characterised as its triflate salt ($[\mathbf{2}][\text{CF}_3\text{SO}_3]_4$) [14].

The photodimerisation of $[\mathbf{1}]^{4+}$ to give $[\mathbf{2}]^{4+}$ upon UV irradiation can be easily monitored by ^1H NMR spectroscopy, see Fig. 2. The [2+2] cycloaddition reaction of the olefinic double bonds is followed by the disappearance of the olefinic protons signal at $\delta = 7.49$ ppm and with the emergence of a new signal at $\delta = 4.99$ ppm which is assigned to the cyclobutane protons. Interestingly, upon formation of $[\mathbf{2}]^{4+}$ diastereotopic protons are observed for the pyridyl groups suggesting a non-equivalent environment. This is in accordance with the X-ray structure analysis of $[\text{Ir}_4(\eta^5\text{-Cp}^*)_4(\mu\text{-oxalato})_2(\mu\text{-tpcb})]^{4+}$ in which the *rctt*-cyclobutane isomer (*rctt*-tetrakis(4-pyridyl)cyclobutane) is observed [11]. Consequently, based on the assumption that the same reactivity takes place here and using multiple one-dimensional and two-dimensional NMR experiments (ROESY, COSY, HSQC) [15], the complete assignment of the tpcb proton signals in cation $[\mathbf{2}]^{4+}$ has been determined, see Fig. 2.

* Corresponding author.

E-mail address: bruno.therrien@unine.ch (B. Therrien).

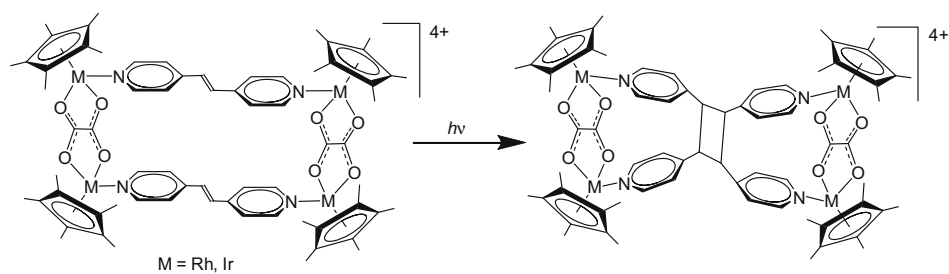
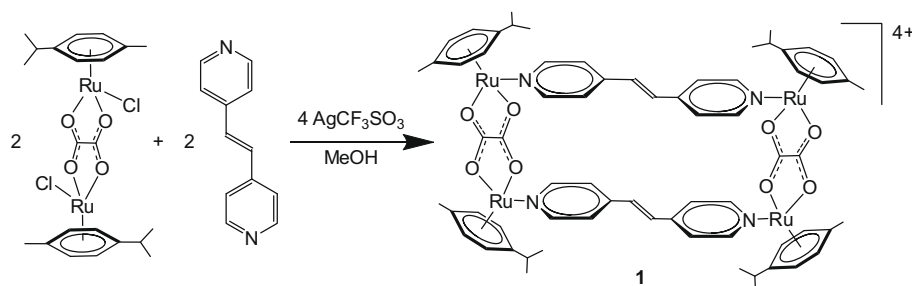
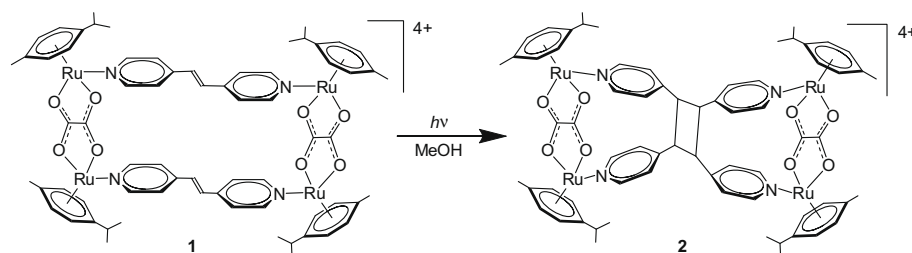


Fig. 1. Single-crystal-to-single-crystal [2+2] cycloaddition in $[M_4(\eta^5\text{-Cp}^*)_4(\mu\text{-oxalato})_2(\mu\text{-bpe})]^{4+}$ to give $[M_4(\eta^5\text{-Cp}^*)_4(\mu\text{-oxalato})_2(\mu\text{-tpcb})]^{4+}$ [11].



Scheme 1.



Scheme 2.

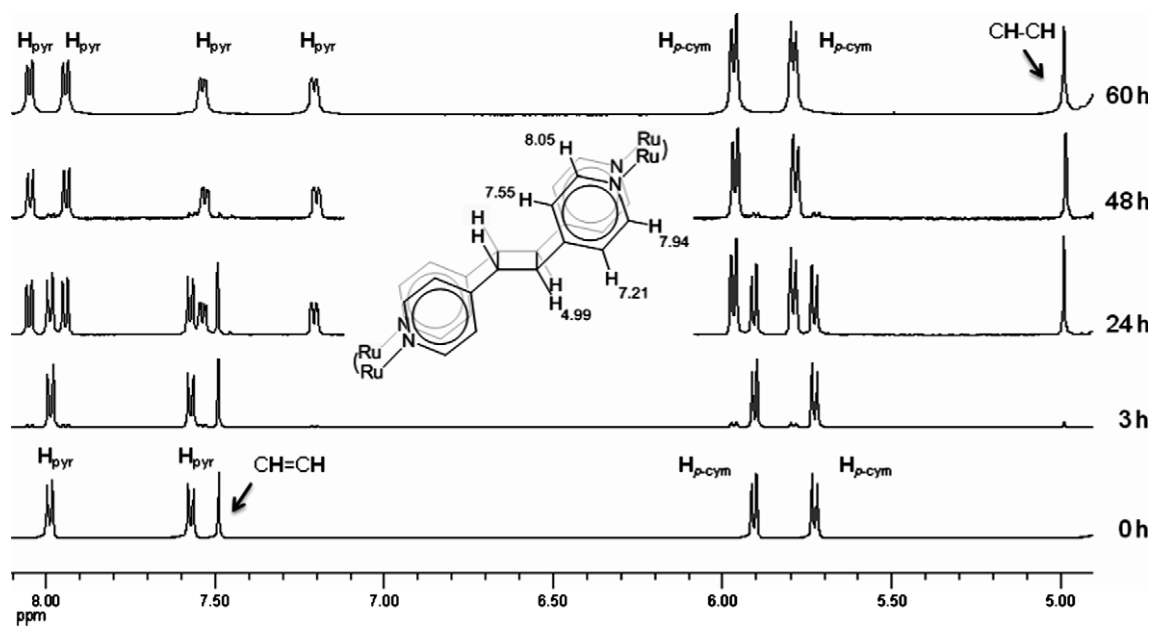


Fig. 2. ^1H NMR spectra (400 MHz, CD_3OD) of the photodimerisation reaction over a 60 h period including the assignment of the *rctt*-tpcb protons.

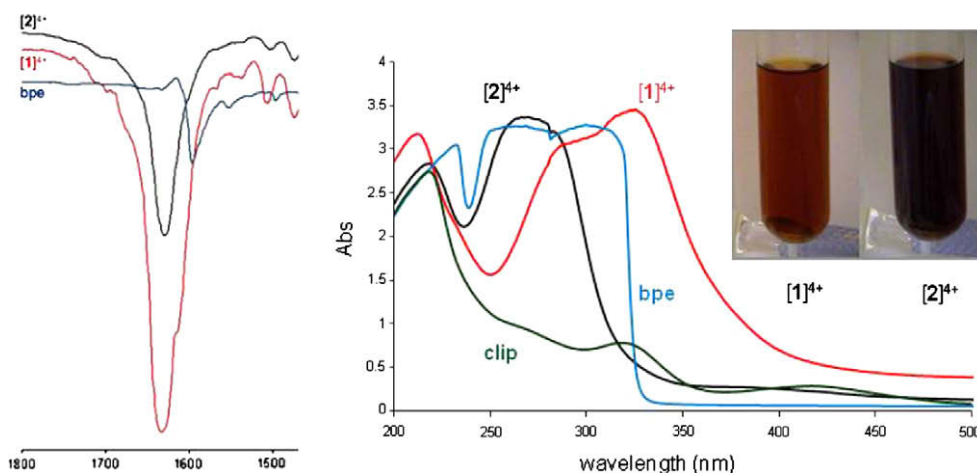


Fig. 3. Infrared (KBr pellets) and UV spectra (10^{-6} M, CH_3OH) of $[\text{Ru}_2(\eta^6\text{-}p\text{-cymene})_2(\mu\text{-oxalato})\text{Cl}_2]$ (clip), bpe, $[\mathbf{1}]^{4+}$ and $[\mathbf{2}]^{4+}$.

The infrared spectra of $[\mathbf{1}][\text{CF}_3\text{SO}_3]_4$ and $[\mathbf{2}][\text{CF}_3\text{SO}_3]_4$ are almost identical and they are dominated by absorptions of the *p*-cymene, pyridyl, and oxalato groups [16]. In addition, strong absorptions attributed to the triflate anions are observed in the infrared spectra at 1262(s), 1029(s) and 638(s) cm^{-1} [17]. It is noteworthy to mention that the band corresponding to the stretching vibration of the bpe ethylene groups ($\nu_{\text{CH}=\text{CH}}$) in $[\mathbf{1}]^{4+}$, centred at 1595(s) cm^{-1} in free bpe [18] and observed as a shoulder in $[\mathbf{1}]^{4+}$, disappears during the formation of $[\mathbf{2}]^{4+}$, as showed in Fig. 3. Moreover, the stretching vibration of the C=O oxalato moieties is observed at 1632 cm^{-1} and remains unchanged after the photochemical cycloaddition.

During the photochemical [2+2] cycloaddition reaction, the initial orange¹ CH_3OH solution of $[\mathbf{1}]^{4+}$ turns dark red upon formation of $[\mathbf{2}]^{4+}$, see inset in Fig. 3. The absorption spectra of $[\text{Ru}_2(\eta^6\text{-}p\text{-cymene})_2(\mu\text{-oxalato})\text{Cl}_2]$ (clip), $[\mathbf{1}]^{4+}$, $[\mathbf{2}]^{4+}$ and uncoordinated bpe are presented in Fig. 3. The absorbance in the electronic spectrum of $[\mathbf{1}]^{4+}$ exhibits two UV transitions which correspond to bpe ($\pi\text{-}\pi^*$) and $[\text{Ru}_2(\eta^6\text{-}p\text{-cymene})_2(\mu\text{-oxalato})\text{Cl}_2]$ (MLCT) transitions [19]. The extinction coefficient attributed to the clip transition increases significantly upon formation of rectangle $[\mathbf{1}]^{4+}$. In $[\mathbf{2}]^{4+}$ a hypsochromic shift of the MLCT transition is observed.

It is well known that in coordinating solvents ligand exchange can easily occur in arene ruthenium complexes. In order to isolate the *rctt*-tetrakis(4-pyridyl)cyclobutane (tpcb) moiety, we heated for 24 h in the presence of triphenylphosphine an acetonitrile solution of $[\mathbf{2}]^{4+}$ [20]. After this period the cleavage of the different connectors is observed and an additional new set of signals appears, among them, two doublets at $\delta = 8.4$ and 7.5 ppm and a singlet at $\delta = 4.5$ ppm which is assigned to free *rctt*-tpcb molecules: This assignment being in accordance with the ^1H NMR values reported for *rctt*-tpcb [21].

In conclusion, we have shown a simple and straightforward synthesis of oxalato-bridged arene ruthenium rectangle using 4,4'-bipyridylethylene connectors. The parallel arrangement of the olefinic double bonds in this supramolecular assembly allows a facile photochemical [2+2] cycloaddition reaction to form the cyclobutane derivative. These data are in agreement with the analogous compounds $[\text{Ir}_4(\eta^5\text{-Cp}^*)_4(\mu\text{-oxalato})_2(\mu\text{-bpe})_2][\text{CF}_3\text{SO}_3]_4$ and $[\text{Ir}_4(\eta^5\text{-Cp}^*)_4(\mu\text{-oxalato})_2(\mu\text{-tpcb})][\text{CF}_3\text{SO}_3]_4$, for which the structures, before and after irradiation, were confirmed by single-crystal X-ray structure analysis [11]. Moreover, if wanted, the *rctt*-tetrakis(4-pyridyl)cyclobutane, the only isomer formed during this photochemical [2+2] cycloaddition, can be recovered.

¹ For interpretation of color in Fig. 3, the reader is referred to the web version of this article.

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- [13] $[\text{Ru}_4(\eta^6\text{-}p\text{-cymene})_4(\mu\text{-oxalato})_2(\mu\text{-bpe})_2][\text{CF}_3\text{SO}_3]_4$: A mixture of AgCF_3SO_3 (149 mg, 0.58 mmol) and $[\text{Ru}_2(\eta^6\text{-}p\text{-cymene})_2(\mu\text{-oxalato})\text{Cl}_2]$ (189 mg, 0.29 mmol) in methanol (50 mL) is stirred at room temperature for 3 h, then filtered to remove AgCl . 4,4'-Bipyridylethylene (53 mg, 0.29 mmol) is therefore added to the filtrate and the solution is stirred at room temperature for 12 h. The solvent is removed and the residue extracted with acetonitrile. The filtrate is concentrated to 2 mL and diethyl ether is added to precipitate **[1]** $[\text{CF}_3\text{SO}_3]_4$ as a light orange powder. Yield: 243 mg (81%). UV-vis (1.0×10^{-6} M, CH_3OH): λ_{max} 325 nm ($\epsilon = 3.45 \times 10^6 \text{ M}^{-1} \text{ cm}^{-1}$), λ_{max} 287 nm ($\epsilon = 3.05 \times 10^6 \text{ M}^{-1} \text{ cm}^{-1}$). IR (KBr, cm^{-1}): 3068 (m, CH aryl), 2969 (m), 1948 (w), 1632 (s, C=O), 1603 (m, C=C), 1434 (m), 1263 (s, CF_3), 1223 (m), 1167 (s), 1029 (s), 843 (m), 638 (s). ^1H NMR (400 MHz, CD_3OD , 298 K): δ (ppm) = 7.99 (d, 8H, $^3J = 6.7$ Hz, H_{pyr}), 7.57 (d, 8H, H_{pyr}), 7.49 (s, 4H, **CH=CH**), 5.95 (d, 8H, $^3J = 6.3$ Hz, $\text{H}_{p\text{-cym}}$), 5.73 (d, 8H, $\text{H}_{p\text{-cym}}$), 2.81 (sept, 4H, $^3J = 6.9$ Hz, **CH**(CH_3)₂), 2.19 (s, 12H, **CH**₃), 1.35 (d, 24H, **CH**(CH_3)₂). ^{13}C NMR (100 MHz, CD_3OD , 298 K): δ (ppm) = 172.4 (C=O), 153.9 (**CH**_{pyr}), 147.7 (**C**_{pyr}), 133.5 (**CH=CH**), 125.1 (**CH**_{pyr}), 103.8 (**C**_{p-cym}), 98.9 (**C**_{p-cym}), 83.5 (**CH**_{p-cym}), 82.8 (**CH**_{p-cym}), 32.5 (**CH**(CH_3)₂), 22.4 (**CH**(CH_3)₂), 18.0 (**CH**₃).
- [14] $[\text{Ru}_4(\eta^6\text{-}p\text{-cymene})_4(\mu\text{-oxalato})_2(\mu\text{-tpcb})][\text{CF}_3\text{SO}_3]_4$: A CD_3OD solution (10 mL) of **[1]** $[\text{CF}_3\text{SO}_3]_4$ (100 mg, 0.05 mmol) is placed next to a Hg lamp (180 W) for 60 h. Then the solvent is removed under vacuum and the red residue washed with dichloromethane (30 mL) to afford **[2]** $[\text{CF}_3\text{SO}_3]_4$. Yield: 83 mg (83 %). UV-vis (1.0×10^{-6} M, CH_3OH): λ_{max} 266 nm ($\epsilon = 3.37 \times 10^6 \text{ M}^{-1} \text{ cm}^{-1}$). IR (KBr, cm^{-1}): 3077 (m, CH aryl), 2969 (m), 1945 (w), 1628 (s, C=O), 1433 (m), 1262 (s, CF_3), 1223 (m), 1165 (s), 1029 (s), 637 (s). ^1H NMR (400 MHz, CD_3OD , 298 K): δ (ppm) = 8.05 (d, 4H, $^3J = 5.9$ Hz, H_{pyr}), 7.94 (d, 4H, $^3J = 5.8$ Hz, H_{pyr}), 7.55 (dd, 4H, $^3J = 5.9$ Hz, $^4J = 1.5$ Hz, H_{pyr}), 7.21 (dd, 4H, H_{pyr}), 5.97 (d, 8H, $^3J = 5.8$ Hz, $\text{H}_{p\text{-cym}}$), 5.79 (d, 8H, $\text{H}_{p\text{-cym}}$), 4.99 (s, 4H, **CH-CH**), 2.84 (sept, 4H, $^3J = 6.9$ Hz, **CH**(CH_3)₂), 2.20 (s, 12H, **CH**₃), 1.35 (d, 24H, **CH**(CH_3)₂). ^{13}C NMR (100 MHz, CD_3OD , 298 K): δ (ppm) = 171.9 (C=O), 154.3 (**CH**_{pyr}), 153.5 (**CH**_{pyr}), 152.9 (**C**_{pyr}), 128.9 (**CH**_{pyr}), 125.6 (**CH**_{pyr}), 103.9 (**C**_{p-cym}), 98.6 (**C**_{p-cym}), 83.2 (**CH**_{p-cym}), 82.8 (**CH**_{p-cym}), 44.9 (**CH-CH**), 32.5 (**CH**(CH_3)₂), 22.5 (**CH**(CH_3)₂), 18.0 (**CH**₃).
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