Published in European Journal of Inorganic Chemistry 5, 725-728, 2010
which should be used for any reference to this work

Designing the Host-Guest Properties of Tetranuclear Arene Ruthenium Metalla-Rectangles to Accommodate a Pyrene Molecule

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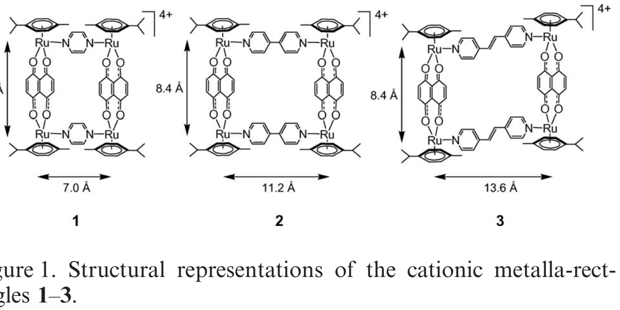
Keywords: Supramolecular chemistry / Host-guest systems / Arene ligands / Ruthenium complexes

Cationic tetranuclear arene ruthenium complexes of the general formula $[Ru_4(p\text{-cymene})_4(N{\cap}N)_2(dhnq)_2]^{4+}$ comprising rectangular structures are obtained in methanol from the reaction of the dinuclear arene ruthenium precursor $[Ru_2(p\text{-cymene})_2(dhnq)_2Cl_2]$ (dhnq = 5,8-dihydroxy-1,4-naphthoquinonato) with pyrazine or bipyridine linkers [$N{\cap}N$ = pyrazine, **1**; 4,4′-bipyridine, **2**; 1,2-bis(4-pyridyl)ethylene, **3**] in the presence of $AgCF_3SO_3$. All complexes **1**–**3**, isolated in good yield as triflate salts, have been characterised by NMR and IR spectroscopy. The interaction of these rectangular complexes with pyrene as a guest molecule has been studied in solution by various NMR techniques (1D, DOSY, ROESY). In [D$_3$]acetonitrile, the pyrazine-containing metalla-rectangle **1** shows no meaningful interactions with pyrene. On the other hand, the 4,4′-bipyridine- and 1,2-bis(4-pyridyl)ethylene-containing metalla-rectangles **2** and **3** clearly interact with pyrene in [D$_3$]acetonitrile. DOSY measurements suggest that, in the case of $[Ru_4(p\text{-cymene})_4(4,4'\text{-bipyridine})_2(dhnq)_2]^{4+}$ (**2**), the interactions occur on the outside of the rectangular assembly, while in the case of $[Ru_4(p\text{-cymene})_4\{1,2\text{-bis(4-pyridyl)ethylene}\}_2(dhnq)_2]^{4+}$ (**3**), the pyrene molecule is found inside the hydrophobic cavity of the metalla-rectangle, thus giving rise to a host-guest system.

Introduction

Arene ruthenium(II) and cyclopentadienyl rhodium(III) or iridium(III) half-sandwich complexes have received considerable attention over the last decade, especially as building blocks in supramolecular chemistry.[1] Their ability to generate a pre-organised arrangement with appropriate multidentate bridging ligands and connectors has allowed the controlled formation of various supramolecular constructions. Indeed, we have used, as well as others, arene ruthenium complexes as building blocks for the assembly of a series of cationic metalla-rectangles containing $OO{\cap}OO$ or $ON{\cap}NO$ bridging ligands ($OO{\cap}OO$ = oxalato, 2,5-dihydroxy-1,4-benzoquinonato, 2,5-dichloro-1,4-benzoquinonato, 6,11-dihydroxy-5,12-naphthacenedionato; $ON{\cap}NO$ = oxonato, 2,5-diarylamino-1,4-benzoquinonato) and polypyridyl ligands [$N{\cap}N$ = pyrazine, 4,4′-bipyridine, 4,7-phenanthroline, 1,2-bis(4-pyridyl)ethylene, 2,5-bis(4-pyridyl)-1,3,5-oxadiazolato] as connectors.[2] The oxalato derivatives $[Ru_4(p\text{-cymene})_4(bpe)_2(oxalato)_2]^{4+}$,[3] $[Rh_4(Cp^*)_4(bpe)_2(oxalato)_2]^{4+}$ and $[Ir_4(Cp^*)_4(bpe)_2(oxalato)_2]^{4+}$ connected with 1,2-bis(4-pyridyl)ethylene (bpe)[4] have shown [2+2] photochemical cycloaddition in solution as well as in the solid state, while the $[M_4(Cp^*)_4(pyrazine)_2(6,11\text{-dihydroxy-5,12-naphthacene-dionato})_2]^{4+}$ (M = Rh, Ir)[5] have been found to encapsulate CH_2Cl_2 or $ClCH_2CH_2Cl$ molecules under single-crystal-to-single-crystal transformation conditions. On the other hand, the $[Ru_4(p\text{-cymene})_4(4,4'\text{-bipyridine})_2(oxonato)_2]^{4+}$ and $[Ru_4(p\text{-cymene})_4(4,7\text{-phenanthroline})_2(oxonato)_2]^{4+}$ metalla-rectangles[6] as well as a series of *p*-cymene and hexamethylbenzene ruthenium metalla-rectangles of the general formula $[Ru_4(arene)_4(N{\cap}N)_2(OO{\cap}OO)_2]^{4+}$ {$OO{\cap}OO$ = 2,5-dihydroxy-1,4-benzoquinonato, 2,5-dichloro-1,4-benzoquinonato; $N{\cap}N$ = pyrazine, 4,4′-bipyridine, 1,2-bis(4-pyridyl)ethylene}[7] have been found to be cytotoxic against cancer cell lines. Herein we report the synthesis and characterisation of a new series of tetranuclear cations incorporating *p*-cymene ruthenium building blocks, bridged by 5,8-dihydroxy-1,4-naphthoquinonato (dhnq) ligands, and connected by pyrazine, 4,4′-bi-



1 **2** **3**

Figure 1. Structural representations of the cationic metalla-rectangles **1**–**3**.

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pyridine or 1,2-bis(4-pyridyl)ethylene bidentate connectors, see Figure 1. Their ability to interact with pyrene in solution has been studied by NMR experiments.

Results and Discussion

Addition of $AgCF_3SO_3$ to the dinuclear complex $[Ru_2(p\text{-cymene})_2(dhnq)Cl_2]$[8] in the presence of $N\cap N$ bidentate ligands {pyrazine, 4,4′-bipyridine or 1,2-bis(4-pyridyl)-ethylene} leads to the formation of the tetranuclear cations $[Ru_4(p\text{-cymene})_4(N\cap N)_2(dhnq)_2]^{4+}$ {$N\cap N$ = pyrazine, **1**; 4,4′-bipyridine, **2**; 1,2-bis(4-pyridyl)ethylene, **3**} in good yield (≈ 75%). These rectangular cations are isolated as their triflate salts [**1**]$[CF_3SO_3]_4$, [**2**]$[CF_3SO_3]_4$ and [**3**]-$[CF_3SO_3]_4$, respectively.

The ^1H NMR spectrum of **1** displays a singlet due to the pyrazine protons. As in free pyrazine, where the proton signal is found at δ = 8.57 in $[D_3]$acetonitrile, the corresponding signal of **1** appears at δ = 8.56 ppm. The ^1H NMR spectrum of **2** shows two doublets due to the 4,4′-bipyridine protons with an upfield shift of 0.24 ppm for the doublet (H_α) found at δ = 8.67 ppm in the free 4,4′-bipyridine in $[D_3]$acetonitrile, the doublet (H_β) at δ = 7.69 ppm being not affected by the coordination to the arene ruthenium units. The same upfield shift is observed with the protons of the 1,2-bis(4-pyridyl)ethylene connector in complex **3**, see Figure 2. Upon formation of the cationic tetranuclear metalla-rectangles, the methyl and isopropyl signals of the *p*-cymene ligands in **1**–**3** remain almost unchanged as compared to complex $[Ru_2(p\text{-cymene})_2(dhnq)Cl_2]$, while the aromatic protons of the *p*-cymene ligands are slightly shifted upfield. However, the proton signal of the 5,8-dihydroxy-1,4-naphthoquinonato bridging ligands in all metalla-rectangles **1**–**3** is shifted downfield as compared to the parent complex $[Ru_2(p\text{-cymene})_2(dhnq)Cl_2]$.[8]

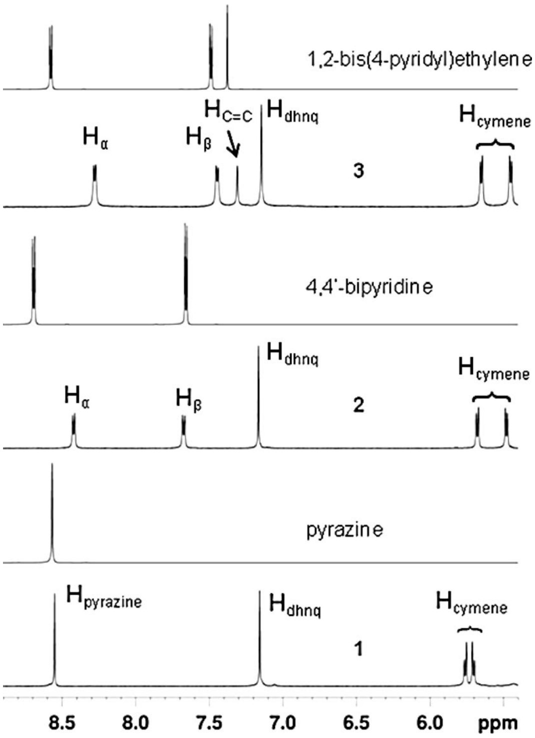

Figure 2. ^1H NMR spectra (400 MHz, CD_3CN) of free pyrazine, 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethylene as well as metalla-rectangles **1**–**3**.

The cavity size of the different metalla-rectangles was estimated from molecular modelling and from analogous structures incorporating the same bridging and connecting ligands. The pyrazine cation **1** possesses a cavity of about about 8.4 × 7.0 Å^2 (Ru–Ru distances), while the cavity size of the bpy and bpe metalla-rectangles **2** and **3** are expected to be approximately 8.4 × 11.2 and 8.4 × 13.6 Å^2, respectively, see Figure 1. Therefore, considering the size of the hydrophobic cavity and the presence of aromatic surfaces in the multiple components of **1**–**3**, we decided to study the host-guest properties of these metalla-rectangles in the presence of pyrene, since pyrene molecule was recently found to interact strongly in the hydrophobic cavity of the metalla-prisms $[Ru_6(p\text{-cymene})_6(tpt)_2(dhnq)_3]^{6+}$ {tpt = 2,4,6-tris(4-pyridyl)-1,3,5-triazine}[8] and $[Ru_6(p\text{-cymene})_6(tpt)_2(dhbq)_3]^{6+}$ (dhbq = 2,5-dihydroxy-1,4-benzoquinonato).[9]

Upon gradual addition of pyrene (0.2–20.0 equiv.) to a CD_3CN solution of metalla-rectangles **1**, **2** and **3** (4.0 mM), the ^1H NMR spectra of **2** and **3** show displacements of the chemical shifts of some of the protons of the host and of the guest, while in the case of **1** no chemical shift changes are observed, see Figure 3. In **2**, the H_β protons of the pyridyl groups are the most affected by the presence of pyrene molecules in solution. Moreover, in **3**, all protons of the $N\cap N$ bidentate ligands as well as the pyrenyl protons are shifted. This suggests different types of interactions between metalla-rectangles **2** and **3** with pyrene in solution.

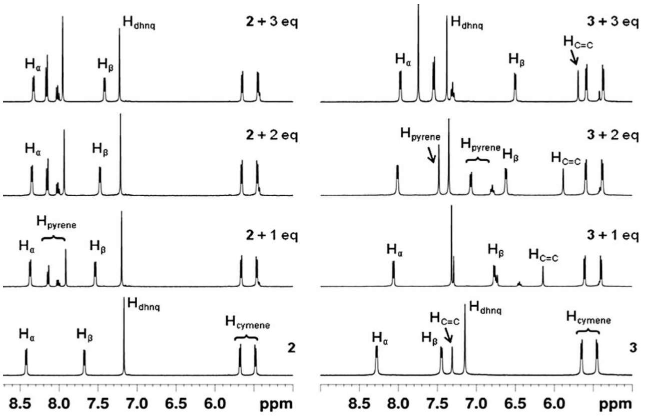

Figure 3. ^1H NMR titrations of pyrene in a CD_3CN solution of [**2**]$[CF_3SO_3]_4$ (left, 4.0 mM, 25 °C) and of [**3**]$[CF_3SO_3]_4$ (right, 4.0 mM, 25 °C).

To gain further insight on the nature of the interactions involved between pyrene and metalla-rectangles **2** and **3**, we performed a series of DOSY measurements.[10] Diffusion-ordered (DOSY) NMR spectroscopy is a valuable tool for investigating large molecules in solution.[11] It is clear from the DOSY spectra of pyrene and **2** (Figure 4) that both compounds keep the same diffusion constant even when mixed together. Therefore, the chemical shifts observed for the host and the guest are attributed to outer interactions.

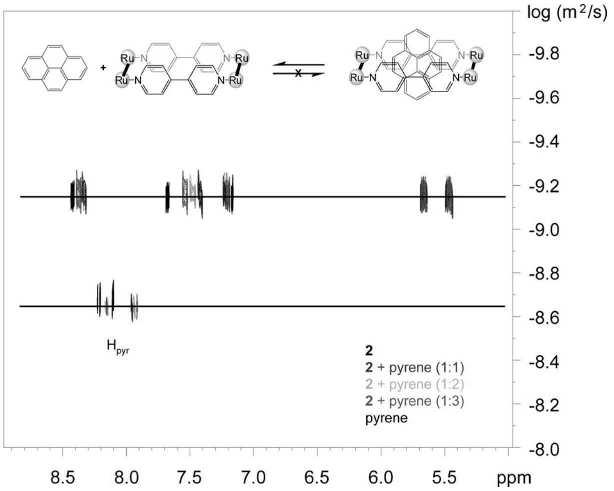

Figure 4. DOSY ^{1}H NMR spectra of pyrene, [**2**][CF_3SO_3]$_4$ and of additional amounts of pyrene (1 to 3 equiv.) to a 4.0 mM solution of [**2**][CF_3SO_3]$_4$.

However, the case of **3** in the interaction with pyrene is totally different. The DOSY spectra show that for a 1:1 mixture of pyrene and [**3**][CF_3SO_3]$_4$ both diffusion coefficients are almost equivalent at about 6.3×10^{-10} $m^2 s^{-1}$ (see Figure 5). Consequently, the pyrene appears to be located in the hydrophobic cavity of **3**, which is in accordance with the strong chemical shift observed for both species in the ^{1}H NMR spectra (Figure 3).

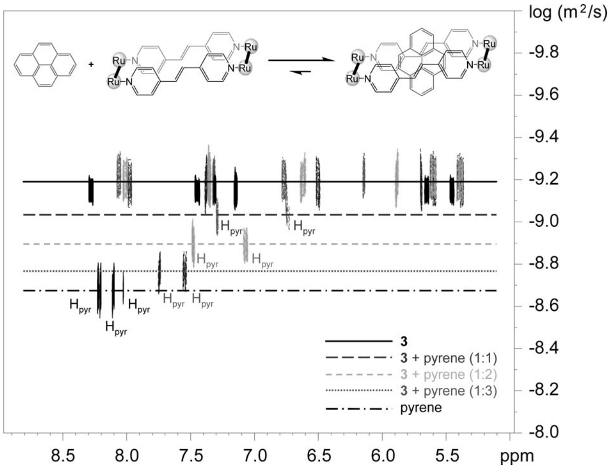

Figure 5. DOSY ^{1}H NMR spectra of pyrene, [**3**][CF_3SO_3]$_4$ and of additional amounts of pyrene (1 to 3 equiv.) to a 4.0 mM solution of [**3**][CF_3SO_3]$_4$.

To confirm the presence of a pyrene molecule in the cavity of metalla-rectangle **3** in solution, one-dimensional ROESY experiments were performed in [D$_3$]acetonitrile. The ROESY experiments were recorded as described previously.[12] As shown in Figure 6, intense cross-peaks are observed between the protons of the pyrene molecule and the protons of the cationic metalla-rectangle **3** in close proximity, especially those of the connecting 1,2-bis(4-pyridyl)ethylene ligands (H_α, H_β and $H_{C=C}$). Therefore, we can conclude that in the case of **3** the pyrene molecule is preferably positioned in the hydrophobic cavity of the metalla-rectangle giving rise to a host-guest system.

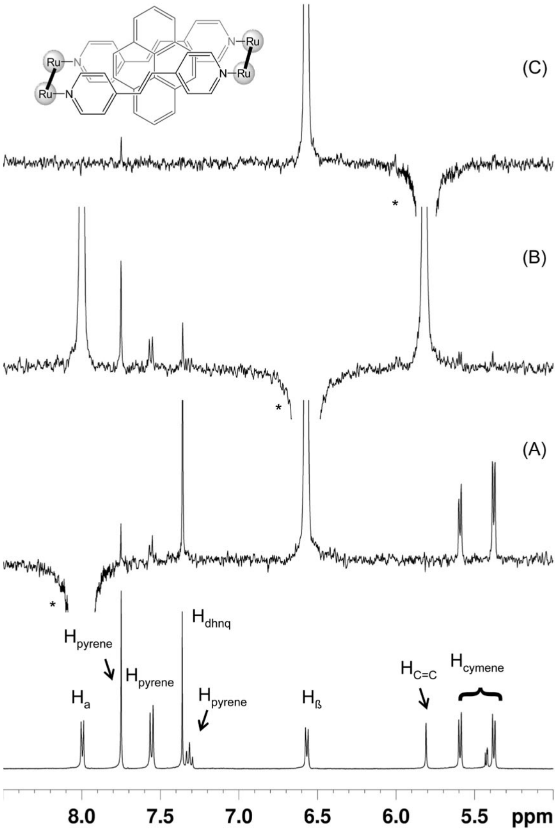

Figure 6. One-dimensional ^{1}H ROESY spectra (400 MHz, CD_3CN, 25 °C) of pyrene and **3** focusing on the 1,2-bis(4-pyridyl)ethylene protons H_α (A), H_β (B) and $H_{C=C}$ (C).

Conclusions

The present study reveals that rectangular-shaped tetranuclear arene ruthenium complexes containing $OO\cap OO$-bridges and $N\cap N$-linkers can be designed to measure by choosing the dimensions of the $N\cap N$-dipyridyl-type ligands in order to accommodate a pyrene guest molecule inside their cavity. In contrast to the carceplex system formed by the metalla-prism [Ru_6(*p*-cymene)$_6$(tpt)$_2$(dhbq)$_3$]$^{6+}$ with pyrene, [pyrene$\subset$$Ru_6$(*p*-cymene)$_6(tpt)_2$(dhbq)$_3$]$^{6+}$, where the guest is permanently encapsulated,[9] the host-guest system formed by metalla-rectangle **3** with pyrene is dynamic and only observed in solution.

Experimental Section

General: [Ru_2(*p*-cymene)$_2$(dhnq)Cl_2] was prepared according to publish methods.[8] All other reagents were commercially available (Sigma–Aldrich) and used as received. The ^{1}H, ^{13}C{^{1}H}, ^{1}H DOSY and ^{1}H ROESY NMR spectra were recorded on a Bruker Avance II 400 spectrometer using the residual protonated solvent as internal standard. Infrared spectra were recorded as KBr pellets on a Perkin–Elmer FTIR 1720 X spectrometer. UV/Vis absorption spectra were recorded on an Uvikon 930 spectrophotometer using precision cells made of quartz (1 cm). Elemental analyses were performed by the Laboratory of Pharmaceutical Chemistry, University of Geneva (Switzerland).

Synthesis of Metalla-Rectangles [1–3][CF$_3$SO$_3$]$_4$: A mixture of [Ru$_2$(*p*-cymene)$_2$(dhnq)Cl$_2$] (0.21 mmol), two equivalents of AgCF$_3$SO$_3$ (0.43 mmol) and one equivalent of the corresponding *N*∩*N* ligand (0.21 mmol) in methanol (40 mL) was stirred at 60 °C for 24 h and then filtered to remove AgCl. The solvent was removed under vacuum and the residue was taken up in dichloromethane (3 mL) and diethyl ether was added to precipitate the product as green or blue solids.

[1][CF$_3$SO$_3$]$_4$: Yield 191 mg, (85%). UV/Vis [1.0×10^{-5} M, (CH$_3$)$_2$CO]: λ_{max} = 306 nm (ε = 3.60×10^{5} M^{-1}cm^{-1}), λ_{max} = 434 nm (ε = 0.27×10^{5} M^{-1}cm^{-1}), λ_{max} = 633 nm (ε = 0.12×10^{5} M^{-1}cm^{-1}), λ_{max} = 692 nm (ε = 0.12×10^{5} M^{-1}cm^{-1}). IR (KBr): $\tilde{\nu}$ = 3066 (w, CH$_{cymene}$), 1538 (s, C=O), 1263 (s, CF$_3$) cm^{-1}. ^{1}H NMR (400 MHz, CD$_3$CN): δ = 8.56 (s, 8 H, H$_{pyrazine}$), 7.17 (s, 8 H, H$_{dhnq}$), 5.77 (d, $^3J_{H,H}$ = 5.7 Hz, 8 H, H$_{cymene}$), 5.72 (d, 8 H, H$_{cymene}$), 2.85 [sept, $^3J_{H,H}$ = 2.8 Hz, 2 H, C**H**(CH$_3$)$_2$], 2.14 (s, 12 H, CH$_3$), 1.47 [d, 24 H, CH(C**H**$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ = 171.0 (**C**O), 148.8 (**C**H$_{pyrazine}$), 137.4 (**C**H$_{dhnq}$), 111.5 (**C**$_{dhnq}$), 105.3 (***C***$_{cymene}$), 100.0 (***C***$_{cymene}$), 84.1 (**C**H$_{cymene}$), 84.0 (**C**H$_{cymene}$), 30.8 [**C**H(CH$_3$)$_2$], 21.9 [CH(**C**H$_3$)$_2$], 16.8 (**C**H$_3$) ppm. C$_{72}$H$_{72}$F$_{12}$N$_4$O$_{20}$Ru$_4$S$_4$ (2073.8): calcd. C 41.70, H 3.49, N 2.70; found C 41.02, H 3.16, N 2.38.

[2][CF$_3$SO$_3$]$_4$: Yield 180 mg, (77%). UV/Vis [1.0×10^{-5} M, (CH$_3$)$_2$CO]: λ_{max} = 306 nm (ε = 3.58×10^{5} M^{-1}cm^{-1}), λ_{max} = 434 nm (ε = 0.25×10^{5} M^{-1}cm^{-1}), λ_{max} = 633 nm (ε = 0.11×10^{5} M^{-1}cm^{-1}), λ_{max} = 692 nm (ε = 0.11×10^{5} M^{-1}cm^{-1}). IR (KBr): $\tilde{\nu}$ = 3070 (w, CH$_{cymene}$), 1536 (s, C=O), 1261 (s, CF$_3$) cm^{-1}. ^{1}H NMR (400 MHz, CD$_3$CN): δ = 8.43 (d, $^3J_{H,H}$ = 8.1 Hz, 8 H, H$_\alpha$), 7.69 (d, 8 H, H$_\beta$), 7.17 (s, 8 H, H$_{dhnq}$), 5.69 (d, $^3J_{H,H}$ = 5.7 Hz, 8 H, H$_{cymene}$), 5.48 (d, 8 H, H$_{cymene}$), 2.83 [sept, $^3J_{H,H}$ = 2.8 Hz, 4 H, C**H**(CH$_3$)$_2$], 2.16 (s, 12 H, CH$_3$), 1.37 [d, 24 H, CH(C**H**$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ = 171.9 (**C**O), 153.9 (**C**H$_\alpha$), 145.8 (**C**$_{bipyridine}$), 138.4 (**C**H$_{dhnq}$), 123.9 (**C**H$_\beta$), 114.8 (**C**$_{dhnq}$), 104.7 (***C***$_{cymene}$), 100.5 (***C***$_{cymene}$), 85.2 (**C**H$_{cymene}$), 84.0 (**C**H$_{cymene}$), 31.5 [**C**H(CH$_3$)$_2$], 23.1 [CH(**C**H$_3$)$_2$], 17.3 (**C**H$_3$) ppm. C$_{84}$H$_{80}$F$_{12}$N$_4$O$_{20}$Ru$_4$S$_4$ (2226.0): calcd. C 45.32, H 3.62, N 2.52; found C 44.82, H 3.48, N 2.42.

[3][CF$_3$SO$_3$]$_4$: Yield 178 mg, (73%). UV/Vis [1.0×10^{-5} M, (CH$_3$)$_2$CO]: λ_{max} = 314 nm (ε = 3.76×10^{5} M^{-1}cm^{-1}), λ_{max} = 438 nm (ε = 0.33×10^{5} M^{-1}cm^{-1}), λ_{max} = 608 nm (ε = 0.14×10^{5} M^{-1}cm^{-1}), λ_{max} = 650 nm (ε = 0.13×10^{5} M^{-1}cm^{-1}), 713 nm (ε = 0.13×10^{5} M^{-1}cm^{-1}). IR (KBr): $\tilde{\nu}$ = 3067 (w, CH$_{cymene}$), 1537 (s, C=O), 1272 (s, CF$_3$) cm^{-1}. ^{1}H NMR (400 MHz, CD$_3$CN): δ = 8.28 (d, $^3J_{H,H}$ = 8.3 Hz, 8 H, H$_\alpha$), 7.45 (d, 8 H, H$_\beta$), 7.31 (s, 4 H, H$_{C=C}$), 7.15 (s, 8 H, H$_{dhnq}$), 5.66 (d, $^3J_{H,H}$ = 7.4 Hz, 8 H, H$_{cymene}$), 5.46 (d, 8 H, H$_{cymene}$), 2.79 [sept, $^3J_{H,H}$ = 2.8 Hz, 4 H, C**H**(CH$_3$)$_2$], 2.17 (s, 12 H, CH$_3$), 1.29 [d, 24 H, CH(C**H**$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ = 171.8 (**C**O), 153.2 (**C**H$_\alpha$), 146.9 (**C**$_{bpe}$), 138.3 (**C**H$_{dhnq}$), 132.1 (**C**$_{C=C}$), 124.2 (**C**H$_\beta$), 112.3 (**C**$_{dhnq}$), 104.5 (***C***$_{cymene}$), 100.2 (***C***$_{cymene}$), 85.1 (**C**H$_{cymene}$), 84.0 (**C**H$_{cymene}$), 31.4 [**C**H(CH$_3$)$_2$], 22.3 [CH(**C**H$_3$)$_2$], 17.3 (**C**H$_3$) ppm. C$_{88}$H$_{84}$F$_{12}$N$_4$O$_{20}$Ru$_4$S$_4$ (2278.0): calcd. C 46.40, H 3.72, N 2.46; found C 45.59, H 3.32, N 2.60.

Acknowledgments

A generous loan of ruthenium chloride hydrate from the Johnson Matthey Technology Centre is gratefully acknowledged.

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