

Synthesis and Photochromic Studies of η^6 -Mesitylene Ruthenium(II) Complexes Bearing N-Heterocyclic Carbene Ligands with Dithienylethene Moiety

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Dedicated to Professor Didier Astruc on the occasion of his 65th birthday

Electronic Supporting Information

X-Ray Crystallography

Crystals of **3** (0.20 × 0.30 × 0.39 mm) and **6** (0.14 × 0.15 × 0.49 mm) mounted in a glass capillary were used for data collection at 305 K on a Bruker Smart CCD 1000 using graphite monochromatized Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Raw frame data were integrated with SAINT program.^[34a] Semi-empirical absorption correction with SADABS^[34b] was applied. The structure was solved by direct methods employing SHELXS-97 program^[34c] and expanded using Fourier techniques. All non-H atoms were refined anisotropically. All of the C-bound H atoms were observable from difference Fourier map but were all placed at geometrical positions with C–H = 0.93, 0.96, 0.97 Å for phenyl, methyl and methylene H-atoms. The positions of H atoms were calculated based on riding mode with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{Carrier})$. For complex **3**, both PF $_6^-$ ions are found to lie about the two-fold axes, while the complex and the water molecule both lie in general positions in the asymmetric unit. For complex **6**, 18 restraints have been used in the refinement since the fluorine atoms in the PF $_6^-$ ion are found to show high rotational disorder. Isotropic restraints with standard deviation of 0.005 for the three fluorine atoms, F1, F2 and F3, in the anisotropic atom displacement components have been used (six restraints for each fluorine atom).

Table S1 Crystal determination data of **3**

Empirical formula	$C_{31}H_{37}ClF_6N_3OPRuS_2 \cdot (H_2O)_{0.5}$	
Formula weight	822.25	
Temperature	305(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	$a = 18.598(7)$ Å	$\alpha = 90^\circ$
	$b = 17.640(7)$ Å	$\beta = 102.867(5)^\circ$
	$c = 22.631(8)$ Å	$\gamma = 90^\circ$
Volume	7238(5) Å ³	
Z	8	
Density (calculated)	1.509 g cm ⁻³	
Absorption coefficient	0.73 mm ⁻¹	
$F(000)$	3352	
Crystal size	0.39 mm × 0.30 mm × 0.20 mm	
Theta range for data collection	1.7 to 28.3°	
Index ranges	$-22 \leq h \leq 20, -21 \leq k \leq 21, -23 \leq l \leq 27$	
Reflections collected	20165	
Independent reflections	6867 [$R_{int} = 0.019$]	
Absorption correction	multi-scan	
Max. and min. transmission	0.868 and 0.764	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6867 / 30 / 437	
Goodness-of-fit on F^2	1.04	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.055, wR_2 = 0.173$	
Largest diff. peak and hole	1.85 and -1.16 e·Å ⁻³	

Table S2 Crystal determination data of **6**

Empirical formula	C ₃₀ H ₃₅ ClF ₆ N ₃ OPRuS ₂ ·H ₂ O	
Formula weight	817.24	
Temperature	305(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	<i>Pbca</i>	
Unit cell dimensions	$a = 17.267(3)$ Å	$\alpha = 90^\circ$
	$b = 14.598(2)$ Å	$\beta = 90^\circ$
	$c = 31.643(5)$ Å	$\gamma = 90^\circ$
Volume	7976(2) Å ³	
Z	8	
Density (calculated)	1.361 g cm ⁻³	
Absorption coefficient	0.66 mm ⁻¹	
<i>F</i> (000)	3328	
Crystal size	0.49 mm × 0.15 mm × 0.14 mm	
Theta range for data collection	1.9 to 25.7°	
Index ranges	$-21 \leq h \leq 20$, $-17 \leq k \leq 17$, $-37 \leq l \leq 38$	
Reflections collected	44148	
Independent reflections	7538 [$R_{\text{int}} = 0.087$]	
Absorption correction	multi-scan	
Max. and min. transmission	0.913 and 0.738	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7538 / 18 / 425	
Goodness-of-fit on F^2	1.14	
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.099$, $wR_2 = 0.272$	
Largest diff. peak and hole	1.14 and -2.26 e·Å ⁻³	

Figure S1 Variable-temperature ^1H NMR spectra of **9** in CDCl_3 (in the region of $\delta = 3.6$ - 9.5 ppm). The asterisk denotes an unknown impurity

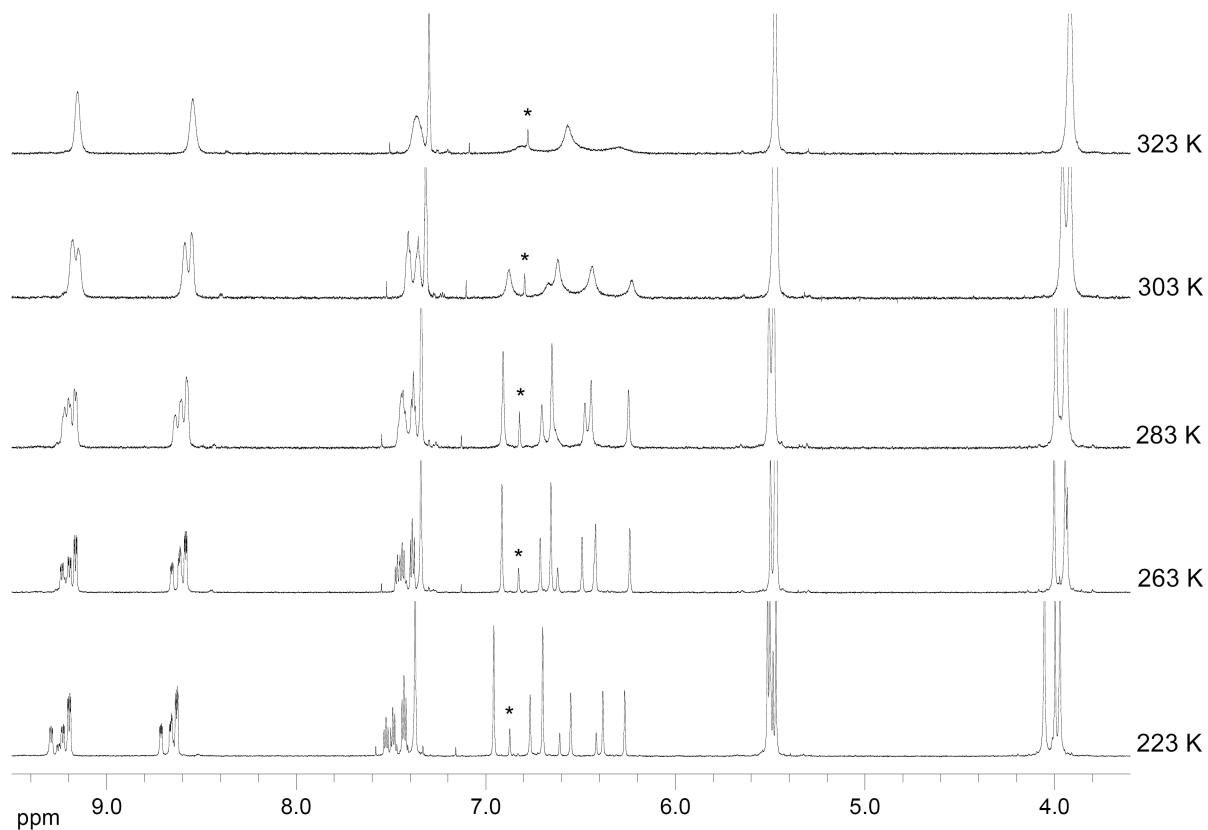


Figure S2 Schematic structure of the four conformations that were involved in the interconversion. The horizontal line represents the plane of the chelating ligand with the *N*-heterocyclic carbene ligand at the front and the imine ligand on the right-hand side. The cross point of the horizontal and vertical lines represents the metal center adopting a quasi-octahedral structure. The quarter-circle represents the mesitylene ring. The two vertical C–H bonds represent protons on the two thiophene rings adopting parallel or anti-parallel conformations. Each conformation exists as a 1:1 mixture of a pair of enantiomers that are not resolvable in the ^1H NMR spectra

