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Christine Viala, Jacques Bonvoisin. Synthesis and characterization of  $\beta$ -diketonato ruthenium(II) complexes with two 4-bromo or protected 4-ethynyl-2,2'-bipyridine ligands. *Inorganica Chimica Acta*, 2010, 363 (7), pp.1409-1414. 10.1016/J.ica.2009.12.057 . hal-01737472

**HAL Id: hal-01737472**

**<https://hal.science/hal-01737472>**

Submitted on 20 Mar 2018

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Synthesis and characterization of  $\beta$ -diketonato ruthenium(II) complexes with two 4-bromo or protected 4-ethynyl-2,2'-bipyridine ligands

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**Abstract :**

Two new mononuclear mixed-ligand ruthenium(II) complexes with acetylacetonate ion (2,4-pentanedionate, acac) and functionalized bipyridine (bpy) in position 4, [Ru(bpyBr)<sub>2</sub>(acac)](PF<sub>6</sub>) (**2**; bpyBr = 4-Bromo-2,2'-bipyridine, acac = 2,4-pentanedionate ion) and [Ru(bpyOH)<sub>2</sub>(acac)](PF<sub>6</sub>) (**3**; bpyOH = 4-[2-methyl-3-butyn-2-ol]-2,2'-bipyridine) were prepared as candidates for building blocks. The <sup>1</sup>H NMR, <sup>13</sup>C-NMR, UV-Vis, electrochemistry and FAB mass spectral data of these complexes are presented.

**Keywords:** Ruthenium(II) bipyridyl complex;  $\beta$ -diketone complex; Acetylenic compounds; Mixed ligand

## Introduction

In the course of finding new building blocks for molecular electronics applications, [1, 2] we turned to mixed-ligands ruthenium(II) complexes with 2,2'-bipyridine and  $\beta$ -diketonato ligands. [3] 2,2'-bipyridine is the most widely used ligand for many reasons. [4] Ruthenium(II) polypyridine complexes have been largely employed due to several intrinsic properties. [5-12] Here we present two novel complexes where bromine or protected alkynyl substituents are connected in position 4 (or 4') of each bipyridine ligands. As well as the synthetic work,  $^1\text{H}$  NMR,  $^{13}\text{C}$ -NMR, UV-Vis, electrochemistry and FAB mass spectral data of these complexes are also described. Particular accent will be devoted to NMR analysis.

## 1. Experimental section

### 2.1. General

All chemicals and solvents were of reagent grade or better. 4-Bromo-2,2'-bipyridine were prepared according to published procedures. [13, 14] The complexes were purified by column chromatography using Aluminium oxide 90 standardized (Merck). Elemental analyses were performed by the Service de microanalyse ICSN-CNRS Gif/Yvette. UV-Visible spectra were recorded on a Varian Cary 5000 spectrophotometer. Cyclic voltammograms were obtained with an Autolab system (PGSTAT100) in  $\text{CH}_2\text{Cl}_2$  (0.1 M tetrabutylammonium hexafluorophosphate, TBAH as supporting electrolyte) at 25°C. A three electrode cell was used comprising a 1 mm Pt-disk working electrode, a Pt wire auxiliary electrode, and an aqueous saturated calomel (SCE) reference electrode. Mass spectra were recorded by the Service de Spectroscopie de Masse of Paul Sabatier University using FAB (Nermag R10-R10, NBA matrix) in positive mode. Analytical thin-layer chromatography (TLC) was performed by using Merck silica gel 60F<sub>254</sub> precoated plates. Preparative HPLC purifications were performed by using a Waters Autopurif apparatus on a 19x150mm Xbridge C18 (5 $\mu\text{m}$ ) column with eluant: 52%/48% of an aqueous solution of Trifluoro-acetic Acid (TFA) 0.1% and methanolic solution of TFA 0.1% for **2** and 45%(0.1%TFA/H<sub>2</sub>O)/55% (0.1%TFA/MeOH) for **3**. Analytical HPLC analyses were performed with an Alliance 2695 pump and a PDA 2996 UV detector.  $^1\text{H}$  NMR and  $^{13}\text{C}$ -NMR spectra were taken on Bruker Avance 300MHz, Bruker Avance 400 MHz, Bruker Avance 500 MHz CryoSonde equipment in  $\text{CD}_3\text{CN}$  solutions at 20°C ( $\text{CD}_3\text{CN}$  at  $\delta\text{H}$ : 1.94,  $\delta\text{C}$ : 1.24). Commercial Ruthenium (III)

chloride hydrate (40-43% Ru)  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  from Strem,  $\alpha$ -D(+)-glucose from Acros were used.  $\text{Ru}(\text{bpy})_2\text{Cl}_2$  was prepared according to Coudret et al. [15]

## 2.2. Synthesis of the complexes

### 2.2.1 Preparation of $[\text{Ru}(\text{bpyBr})_2\text{Cl}_2]$ (**1**).

In a Schlenk tube containing a degassed ethanediol-boiled water solution (12/4 mL) was added  $\text{RuCl}_3$  (1.77 g, 7.3 mmol) under Argon. The mixture was kept at 80°C for 15 mn, then 4-Bromo-2,2'-bipyridine (3.40 g, 14.4 mmol) was added and the temperature was raised to 100°C, then glucose (0.20 g, 1.1 mmol) was added, then a black precipitate appeared on the flask. After 10 mn of stirring, L-ascorbic acid (0.49 g, 2.8 mmol) was added. The solution turned violet and an abundant precipitate was quickly formed. The heating was stopped after 30 mn then the mixture was cooled down at 0°C. The crude product is then recovered by filtration. It was washed with a mixture of ether/acetone at a ratio 85:15 (200 mL) then with ether/acetone at a ratio 80:20 (100 mL) and finally ether (100 mL). The title complex was obtained as a microcrystalline dark red powder (3.94 g, 84 %). Mass spectroscopy (FAB, DCM, MNBA) m/z: positive mode: 642  $[\text{M}]^+$  (calc. 639.8).

### 2.2.2. Preparation of $[\text{Ru}(\text{bpyBr})_2(\text{acac})](\text{PF}_6)$ (**2**).

To a degassed boiled water solution (100 mL) was added  $[\text{Ru}(\text{bpyBr})_2\text{Cl}_2]$  **1** (3.92 g, 6.1 mmol), it was then stirred for 5 mn. Degassed 2,4-pentanedionate ion (7.97 mL, 115.6 mmol) was added, then KOH (0.34 g, 6 mmol), the solution was kept at reflux for 6 h. It was then cool down and  $\text{NH}_4\text{PF}_6$  (0.98 g, 6 mmol) was added. A dark violet precipitate was obtained. After filtration, the solid was solubilised in  $\text{CH}_2\text{Cl}_2$  and purified by precipitation in a mixture of ether/hexane (20:80). This process was repeated twice in order to obtain the title complex as a dark red microcrystalline powder (4.51 g, 90.6%).

Anal. Calcd. % for  $\text{C}_{25}\text{H}_{21}\text{Br}_2\text{F}_6\text{N}_4\text{O}_2\text{PRu}$ : C, 36.8; H, 2.6; N, 6.9. Found: C, 37.1; H, 2.6; N, 6.7. Mass spectroscopy (FAB, DCM, MNBA) m/z: positive mode: 671  $[\text{M} + \text{PF}_6]^+$  (calc. 668.9). CV (DCM, 0.1M TBAH, 0.1Vs<sup>-1</sup>, vs SCE)  $E_{1/2}(\text{RuII}/\text{RuIII}) = 0.76$  V,  $\Delta E = 0.073$  V. ( $\alpha$  form) cf scheme 3 <sup>1</sup>H RMN ( $\text{CD}_3\text{CN}$ )  $\delta$ : 1.79 (6H, s,  $\text{H}_A$ ); 5.39 (1H, s,  $\text{H}_B$ ); 7.29 (2H, dd,  $J_{e/f}=6.2\text{Hz}$ ,  $J_{e/c}=2.1\text{Hz}$ ,  $\text{H}_c$ ); 7.57 (2H, d,  $J_{f/e}=6.2\text{Hz}$ ,  $\text{H}_f$ ); 7.65 (2H, ddd,  $J_{e/d\sigma}=7.2\text{Hz}$ ,  $J_{e/f\sigma}=5.6\text{Hz}$ ,  $J_{e/c\sigma}=1.1\text{Hz}$ ,  $\text{H}_{e\sigma}$ ); 8.09 (2H, ddd,  $J_{d\sigma/e\sigma}=7.9\text{Hz}$ ,  $J_{d\sigma/c\sigma}=7.9\text{Hz}$ ,  $J_{d\sigma/f\sigma}=1.5\text{Hz}$ ,  $\text{H}_{d\sigma}$ ); 8.46 (2H, d,  $J_{c\sigma/d\sigma}=8.1\text{Hz}$ ,  $\text{H}_{c\sigma}$ ); 8.55 (2H, d,  $J_{c/e}=2.0\text{Hz}$ ,  $\text{H}_c$ ); 8.66 (2H, ddd,  $J_{f\sigma/e\sigma}=5.5\text{Hz}$ ,

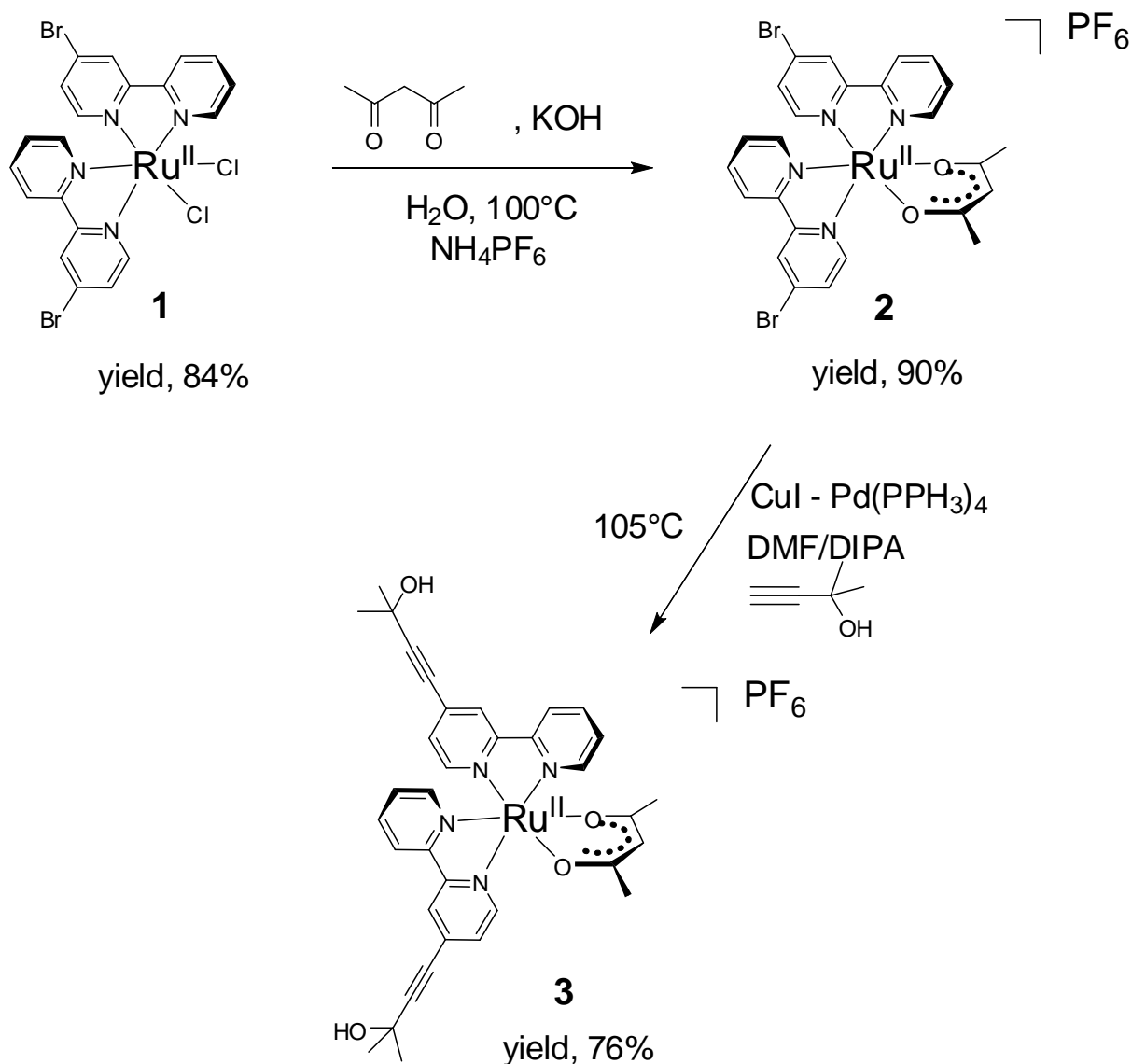
$J_{f\delta} = 1.5 \text{ Hz}$ ,  $J_{f\epsilon} = 0.9 \text{ Hz}$ ,  $H_f$ ).  $^{13}\text{C}$  RMN ( $\text{CD}_3\text{CN}$ )  $\delta$ : 27.85 (A $\delta$ ); 100.39 (B); 124.49 (c $\delta$ ); 127.33 (c); 127.67 (e $\delta$ ); 129.13 (e); 131.20 (d); 137.49 (d $\delta$ ); 151.32 (f  $\delta$ ); 154.75 (f); 157.64 (b $\delta$ ); 161.27 (b); 187.66 ( $\gamma'$ ). ( **$\beta$  form**)  $^1\text{H}$  RMN ( $\text{CD}_3\text{CN}$ )  $\delta$ : 1.78 (3H, s,  $H_A$ ); 1.80 (3H, s,  $H_{A'}$ ); 5.39 (1H, s,  $H_B$ ); 7.15 (1H, ddd,  $J_{5\delta/4\delta} = 7.3 \text{ Hz}$ ,  $J_{5\delta/6\delta} = 5.7 \text{ Hz}$ ,  $J_{5\delta/3\delta} = 1.3 \text{ Hz}$ ,  $H_{5\delta}$ ); 7.29 (1H, dd,  $J_{e/f} = 6.2 \text{ Hz}$ ,  $J_{e/c} = 2.1 \text{ Hz}$ ,  $H_e$ ); 7.63 (1H, dd,  $J_{f/e} = 6.2 \text{ Hz}$ ,  $J_{f/c} = 0.4 \text{ Hz}$ ,  $H_f$ ); 7.66 (1H, ddd,  $J_{e\delta/d\delta} = 7.5 \text{ Hz}$ ,  $J_{e\delta/f\delta} = 5.6 \text{ Hz}$ ,  $J_{e\delta/c\delta} = 1.2 \text{ Hz}$ ,  $H_{e\delta}$ ); 7.73 (1H, ddd,  $J_{6\delta/5\delta} = 5.7 \text{ Hz}$ ,  $J_{6\delta/4\delta} = 1.4 \text{ Hz}$ ,  $J_{6\delta/3\delta} = 0.8 \text{ Hz}$ ,  $H_{6\delta}$ ); 7.79 (2H, m,  $H_5$  et  $H_{4\delta}$ ); 8.10 (1H, ddd,  $J_{d\delta/c\delta} = 8.1 \text{ Hz}$ ,  $J_{d\delta/e\delta} = 7.7 \text{ Hz}$ ,  $J_{d\delta/f\delta} = 1.5 \text{ Hz}$ ,  $H_{d\delta}$ ); 8.35 (1H, m,  $H_{3\delta}$ ); 8.47 (2H, m,  $H_{c\delta}$  et  $H_6$ ); 8.55 (1H, d,  $J_{c/e} = 2.0 \text{ Hz}$ ,  $H_c$ ); 8.68 (2H, m,  $H_{f\delta}$  et  $H_3$ ).  $^{13}\text{C}$  RMN ( $\text{CD}_3\text{CN}$ )  $\delta$ : 27.84 (A and A'); 100.46 (B); 124.51 (3 $\delta$ ); 124.60 (c $\delta$ ); 126.73 (5 $\delta$ ); 127.37 (3); 127.47 (c); 127.66 (e $\delta$ ); 129.13 (e); 130.12 (5); 131.21 (d); 123.91 (4); 136.14 (4 $\delta$ ); 137.51 (d $\delta$ ); 151.34 (f  $\delta$ ); 151.83 (6); 154.47 (6 $\delta$ ); 154.81 (f); 157.50 (b $\delta$ ); 158.78 (2 $\delta$ ); 159.80 (2); 161.25 (b); 187.71 ( $\gamma'$ ); 187.76 ( $\gamma$ ). ( **$\gamma$  form**)  $^1\text{H}$  RMN ( $\text{CD}_3\text{CN}$ )  $\delta$ : 1.77 (6H, s,  $H_A$ ); 5.38 (1H, s,  $H_B$ ); 7.14 (2H, ddd,  $J_{5\delta/4\delta} = 7.4 \text{ Hz}$ ,  $J_{5\delta/6\delta} = 5.6 \text{ Hz}$ ,  $J_{5\delta/3\delta} = 1.3 \text{ Hz}$ ,  $H_{5\delta}$ ); 7.79 (6H, m,  $H_{6\delta}$ ,  $H_{4\delta}$ ,  $H_5$ ); 8.36 (2H, m,  $H_{3\delta}$ ); 8.48 (2H, d,  $J_{6/5} = 6.1 \text{ Hz}$ ,  $H_6$ ); 8.71 (2H, d,  $J_{3/5} = 1.9 \text{ Hz}$ ,  $H_3$ ).  $^{13}\text{C}$  RMN ( $\text{CD}_3\text{CN}$ )  $\delta$ : 27.86 (A); 100.48 (B); 124.61 (3 $\delta$ ); 126.69 (5 $\delta$ ); 127.38 (3); 130.08 (5); 132.82 (4); 136.11 (4 $\delta$ ); 151.76 (6); 154.45 (6 $\delta$ ); 158.91 (2 $\delta$ ); 159.76 (2); 187.76 ( $\gamma$ )

### 2.2.3. Preparation of $[\text{Ru}(\text{bpyOH})_2(\text{acac})](\text{PF}_6)$ (**3**).

In a Schlenk tube,  $[\text{Ru}(\text{bpyBr})_2(\text{acac})](\text{PF}_6)$  **2** (1 g, 1.23 mmol), 2-methyl-3-butyn-2-ol (1 ml, 10.2 mmol), CuI (0.007 g, 0.037 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.007 g, 0.006 mmol), diisopropylamine (DIPA) (2.4 mL, 16.9 mmol) were placed in solution in previously degassed anhydrous DMF (15 mL). The reaction mixture was kept at  $105^\circ\text{C}$  for 3 h, the reaction was followed by TLC on  $\text{Al}_2\text{O}_3$  gel 60 F254  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  (50:50). The solution was then cooled down and the product was precipitated in a round flask containing 250 mL of ether/hexane (40:60). After filtration, the crude was dissolved in  $\text{CH}_2\text{Cl}_2$  and precipitated again. This was repeated three times. The residue was purified by column chromatography ( $\text{Al}_2\text{O}_3$  90 A; solvent,  $\text{CH}_2\text{Cl}_2$ ; eluent,  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  (2:1)). **3** was obtained as a dark red microcrystalline powder (0.77 g, 76 %).

Mass spectroscopy (FAB, DCM, MNBA) m/z: positive mode: 677  $[\text{M} + \text{PF}_6]^+$  (calc. 677.2). CV (DCM, 0.1M TBAH,  $0.1 \text{ V s}^{-1}$ , vs SCE)  $E_{1/2}(\text{RuII}/\text{RuIII}) = 0.73 \text{ V}$ ,  $\Delta E = 0.074 \text{ V}$ . ( **$\alpha$  form**) cf scheme 4  $^1\text{H}$  RMN ( $\text{CD}_3\text{CN}$ )  $\delta$ : 1.52 (12H, s,  $H_D$ ); 1.80 (6H, s,  $H_A$ ); 3.60 (2H, s,  $H_{\text{OH}}$ ); 5.40 (1H, s,  $H_B$ ); 7.01 (2H, dd,  $J_{e/f} = 6.0 \text{ Hz}$ ,  $J_{e/c} = 1.8 \text{ Hz}$ ,  $H_e$ ); 7.65 (4H, m,  $H_{e\delta}$  et  $H_f$ ); 8.09 (2H, ddd,  $J_{d\delta/e\delta} = 8.1 \text{ Hz}$ ,  $J_{d\delta/c\delta} = 7.6 \text{ Hz}$ ,  $J_{d\delta/f\delta} = 1.5 \text{ Hz}$ ,  $H_{d\delta}$ ); 8.29 (2H, dd,  $J_{c/e} = 1.8 \text{ Hz}$ ,

$J_{c/f}=0.6$  Hz,  $H_c$ ); 8.45 (2H, m,  $H_{c\emptyset}$ ); 8.64 (2H, ddd,  $J_{f\emptyset e\emptyset}=5.7$  Hz,  $J_{f\emptyset d\emptyset}=1.5$  Hz,  $J_{f\emptyset c\emptyset}=0.8$  Hz,  $H_{f\emptyset}$ ).  $^{13}\text{C}$  RMN ( $\text{CD}_3\text{CN}$ )  $\delta$ : 27.86 ( $A\emptyset$ ); 31.33 ( $D\emptyset$ ); 65.59 ( $F\emptyset$ ); 78.68 ( $G\emptyset$ ); 100.35 ( $B$ ); 103.19 ( $E\emptyset$ ); 124.16 ( $c\emptyset$ ); 125.60 ( $c$ ); 127.38 ( $e\emptyset$ ); 127.29 ( $e$ ); 130.16 ( $d$ ); 137.46 ( $d\emptyset$ ); 151.15 ( $f\emptyset$ ); 154.07 ( $f$ ); 158.19 ( $b\emptyset$ ); 160.32 ( $b$ ); 187.65 ( $\gamma\emptyset$ ). ( **$\beta$  form**)  $^1\text{H}$  RMN ( $\text{CD}_3\text{CN}$ )  $\delta$ : 1.52 (6H, s,  $H_{D\emptyset}$ ); 1.60 (6H, s,  $H_D$ ); 1.78 (3H, s,  $H_A$ ); 1.80 (3H, s,  $H_{A\emptyset}$ ); 3.57 (1H, s,  $H_{OH\emptyset}$ ); 3.67 (1H, s,  $H_{OH}$ ); 5.39 (1H, s,  $H_B$ ); 7.00 (1H, dd,  $J_{e/f}=6.0$  Hz,  $J_{e/c}=1.6$  Hz,  $H_e$ ); 7.13 (1H, ddd,  $J_{5\emptyset 4\emptyset}=7.2$  Hz,  $J_{5\emptyset 6\emptyset}=5.8$  Hz,  $J_{5\emptyset 3\emptyset}=1.1$  Hz,  $H_{5\emptyset}$ ); 7.54 (1H, dd,  $J_{5/6}=5.8$  Hz,  $J_{5/3}=1.7$  Hz,  $H_5$ ); 7.66 (1H, ddd,  $J_{e\emptyset d\emptyset}=7.3$  Hz,  $J_{e\emptyset f\emptyset}=5.6$  Hz,  $J_{e\emptyset c\emptyset}=1.0$  Hz,  $H_{e\emptyset}$ ); 7.71 (2H, m,  $H_f$  et  $H_{6\emptyset}$ ); 7.79 (1H, ddd,  $J_{4\emptyset 5\emptyset}=8.0$  Hz,  $J_{4\emptyset 3\emptyset}=7.8$  Hz,  $J_{4\emptyset 6\emptyset}=1.3$  Hz,  $H_{4\emptyset}$ ); 8.09 (1H, ddd,  $J_{d\emptyset e\emptyset}=7.9$  Hz,  $J_{d\emptyset c\emptyset}=7.8$  Hz,  $J_{d\emptyset f\emptyset}=1.3$  Hz,  $H_{d\emptyset}$ ); 8.28 (1H, d,  $J_{c/e}=1.7$  Hz,  $H_c$ ); 8.34 (1H, d,  $J_{3\emptyset 4\emptyset}=8.1$  Hz,  $H_{3\emptyset}$ ); 8.43 (1H, d,  $J_{3/5}=1.5$  Hz,  $H_3$ ); 8.46 (1H, d,  $J_{c\emptyset d\emptyset}=8.2$  Hz,  $H_{c\emptyset}$ ); 8.61 (1H, d,  $J_{6/5}=5.8$  Hz,  $H_6$ ); 8.67 (1H, m,  $H_{f\emptyset}$ ).  $^{13}\text{C}$  RMN ( $\text{CD}_3\text{CN}$ )  $\delta$ : 27.85 ( $A$  and  $A\emptyset$ ); 31.33 ( $D\emptyset$ ); 31.38 ( $D$ ); 65.59 ( $F\emptyset$ ); 65.67 ( $F$ ); 78.68 ( $G\emptyset$ ); 78.94 ( $G$ ); 100.39 ( $B$ ); 103.13 ( $E\emptyset$ ); 103.37 ( $E$ ); 124.14 ( $C\emptyset$ ); 124.22 ( $3\emptyset$ ); 125.59 ( $C$ ); 125.71 ( $3$ ); 126.50 ( $5\emptyset$ ); 127.35 ( $e\emptyset$ ); 127.38 ( $e$ ); 128.42 ( $5$ ); 130.05 ( $d$ ); 131.68 ( $4$ ); 136.13 ( $4\emptyset$ ); 137.46 ( $d\emptyset$ ); 151.08 ( $6$  and  $f\emptyset$ ); 154.08 ( $6\emptyset$ ); 154.21 ( $f$ ); 158.08 ( $b\emptyset$ ); 158.87 ( $2$ ); 159.48 ( $2\emptyset$ ); 160.34 ( $b$ ); 187.63 ( $\gamma\emptyset$ ); 187.65 ( $\gamma$ ). ( **$\gamma$  form**)  $^1\text{H}$  RMN ( $\text{CD}_3\text{CN}$ )  $\delta$ : 1.61 (12H, s,  $H_D$ ); 1.79 (6H, s,  $H_A$ ); 3.67 (2H, s,  $H_{OH}$ ); 5.39 (1H, s,  $H_B$ ); 7.12 (2H, ddd,  $J_{5\emptyset 4\emptyset}=7.3$  Hz,  $J_{5\emptyset 6\emptyset}=5.8$  Hz,  $J_{5\emptyset 3\emptyset}=1.3$  Hz,  $H_{5\emptyset}$ ); 7.55 (2H, dd,  $J_{5/6}=5.8$  Hz,  $J_{5/4}=1.7$  Hz,  $H_5$ ); 7.77 (4H, m,  $H_{6\emptyset}$  et  $H_{4\emptyset}$ ); 8.34 (2H, d,  $J_{3\emptyset 4\emptyset}=8.1$  Hz,  $H_{3\emptyset}$ ); 8.43 (2H, d,  $J_{3/5}=1.5$  Hz,  $H_3$ ); 8.64 (2H, dd,  $J_{6/5}=5.8$  Hz,  $J_{6/3}=0.5$  Hz,  $H_6$ ).  $^{13}\text{C}$  RMN ( $\text{CD}_3\text{CN}$ )  $\delta$ : 27.84 ( $A$ ); 31.38 ( $D$ ); 65.67 ( $F$ ); 78.95 ( $G$ ); 100.44 ( $B$ ); 103.34 ( $E$ ); 124.23 ( $3\emptyset$ ); 125.69 ( $3$ ); 126.47 ( $5\emptyset$ ); 128.44 ( $5$ ); 131.69 ( $4$ ); 136.03 ( $4\emptyset$ ); 151.01 ( $6$ ); 154.23 ( $6\emptyset$ ); 158.76 ( $2$ ); 159.50 ( $2\emptyset$ ); 187.64 ( $\gamma$ ).



**Scheme 1**

## 2. Results and discussion

$\text{Ru}(\text{bpyBr})_2\text{Cl}_2$  **1** was prepared by the method of Coudret et al. [15] The synthesis of complexes **2** and **3** follows the procedure given in scheme 1. **3** was prepared by a Sonogashira cross-coupling reaction [16] between the Bromoruthenium complex **2** and 1-butynol under classic conditions ( $\text{CuI}$ ,  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{DMF/DIPA}$ ).

Cyclic voltammetry (CV) data for the complexes is given in Table 1. The  $E_{1/2}$  potentials were determined from the average of the anodic and cathodic peak potentials. All the waves are reversible with peak to peak separation of around 70-75 mV. A positive shift of around 0.3 V is observed when going from **1** to **2** or **3** due to the substitution of two chloride anions by just one acetylacetonato anionic ligand. The reversible half-wave potentials  $E_{1/2}$  of **2-3** are

very close to each other ( $\Delta E(\mathbf{2-3}) = 27\text{mV}$ ) and also close to those observed for  $[\text{Ru}(\text{bpd})(\text{bpy})_2](\text{PF}_6)$  (bpd = 3-Bromo-2,4-pentanedionate ion) (0.752V) and  $[\text{Ru}(\text{tipsepd})(\text{bpy})_2](\text{PF}_6)$  (tipsepd = 3-((Triisopropylsilyl)ethynyl)-2,4-pentanedionate ion) (0.743V). [3] By comparing the redox potentials of **2** and **3** to the one of  $[\text{Ru}(\text{acac})(\text{bpy})_2](\text{PF}_6)$  (0.678 V) [3], one can observe that the positive shift of around 80 mV which reflects the electron-withdrawing character of  $\delta\text{Br}$  or  $-\text{C} \equiv \text{C}(\text{CH}_3)_2\text{OH}$  is the same than the one previously observed for  $\text{Ru}(\text{bpd})(\text{bpy})_2](\text{PF}_6)$  and  $[\text{Ru}(\text{tipsepd})(\text{bpy})_2](\text{PF}_6)$ . Indeed, whatever the substituents (Br or protected alkynyl group) and the position of these substituents ( $\gamma$ -position of the  $\beta$ -diketonato or position 4 of the bipyridine ligand) are, the electronic effect is the same.

**Table 1**

UV-Vis and electrochemical data

Complex	UV-Vis data <sup>a</sup> $\lambda/\text{nm}$ ( $\epsilon/10^3 \text{ M}^{-1}\text{cm}^{-1}$ )	Redox potentials <sup>b</sup> $E_{1/2}/\text{V}$ ( $\Delta E$ , V)
<b>1</b>	236 (26.5), 292sh (28.7), 300 (33.9), 384 (7.1), 496sh (3.5), 570 (5.8)	+0.445 (0.073)
<b>2</b>	233 (39.5), 251 (33.5), 268sh (32), 278sh (34.2), 291sh (48.5), 298 (63.8), 381 (13.8), 535 (11.4), 586sh (8.2)	+0.757 (0.073)
<b>3</b>	253 (50.3), 268sh (39.7), 298sh (34.9), 307 (49.2), 391 (11.9), 537 (12.1), 585sh (8)	+0.730 (0.074)

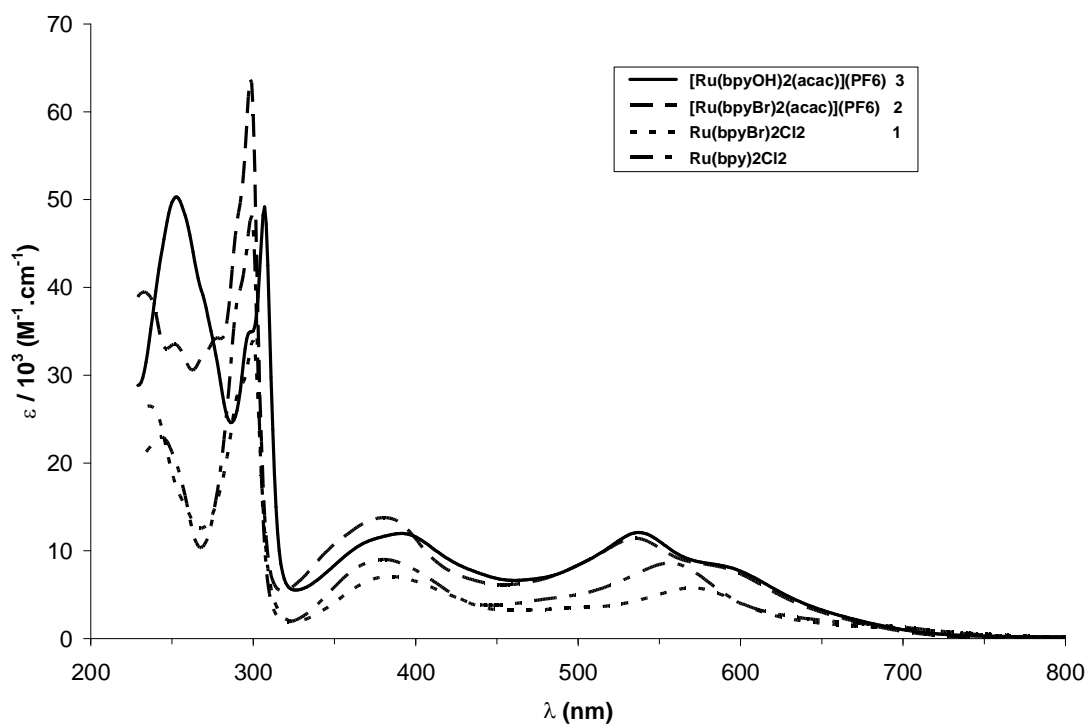
<sup>a</sup> In  $\text{CH}_2\text{Cl}_2$

<sup>b</sup> Versus SCE, in  $\text{CH}_2\text{Cl}_2$ , 0.1M TBAH, 0.1V/s

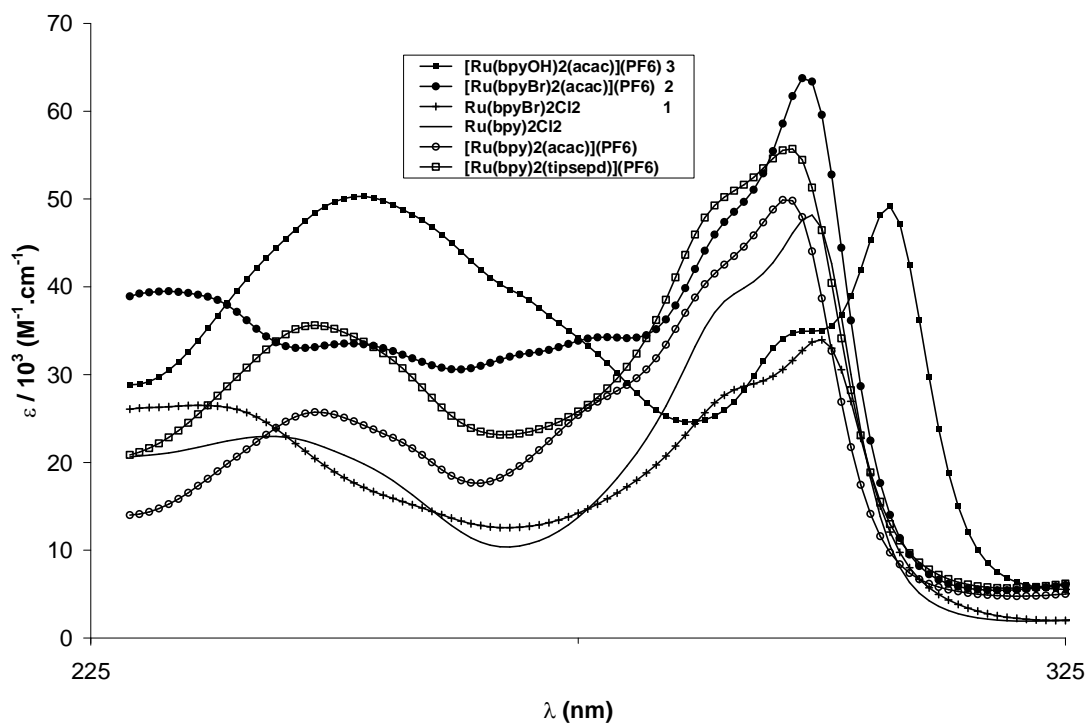
The UV-Vis data are shown in Table 1 and Fig 1-2. In the visible region, for **2** and **3** one can observe three transitions probably attributed to MLCT transitions as it has already been observed in mixed-ligand Ru(II) complexes with bpy and  $\beta$ -diketonato type ligand.[3] One can notice that the two bands around 580 and 530 nm collapse to just one band (570 nm) when going from **2-3** to **1**. In the UV region, (*cf* Fig 2) there is mostly two strong bands for all compounds attributed to  $\pi \rightarrow \pi^*$  intra ligand (IL) but two points have to be noted: When going from **1-2** to **3**, the transition at 300 nm is red shifted to 307 nm. A hyperchromic effect is observed for the absorption band located around 250 nm going from  $[\text{Ru}(\text{tipsed})(\text{bpy})_2](\text{PF}_6)$



to **3** from 35600 to 50300  $M^{-1}cm^{-1}$  (increase by a factor of 1.4), this corroborates the prior attribution to the CC triple bond character. [3]

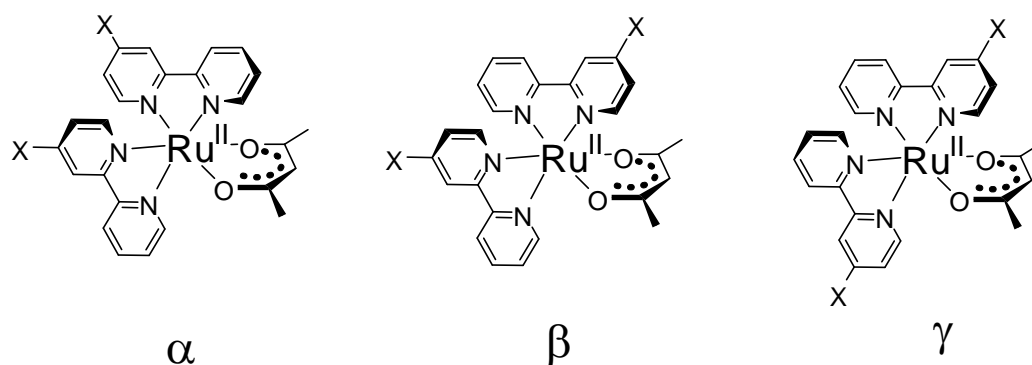


**Figure 1.** UV-Vis spectra of complexes  $Ru(bpy)_2Cl_2$ , **1**, **2** and **3** in  $CH_2Cl_2$



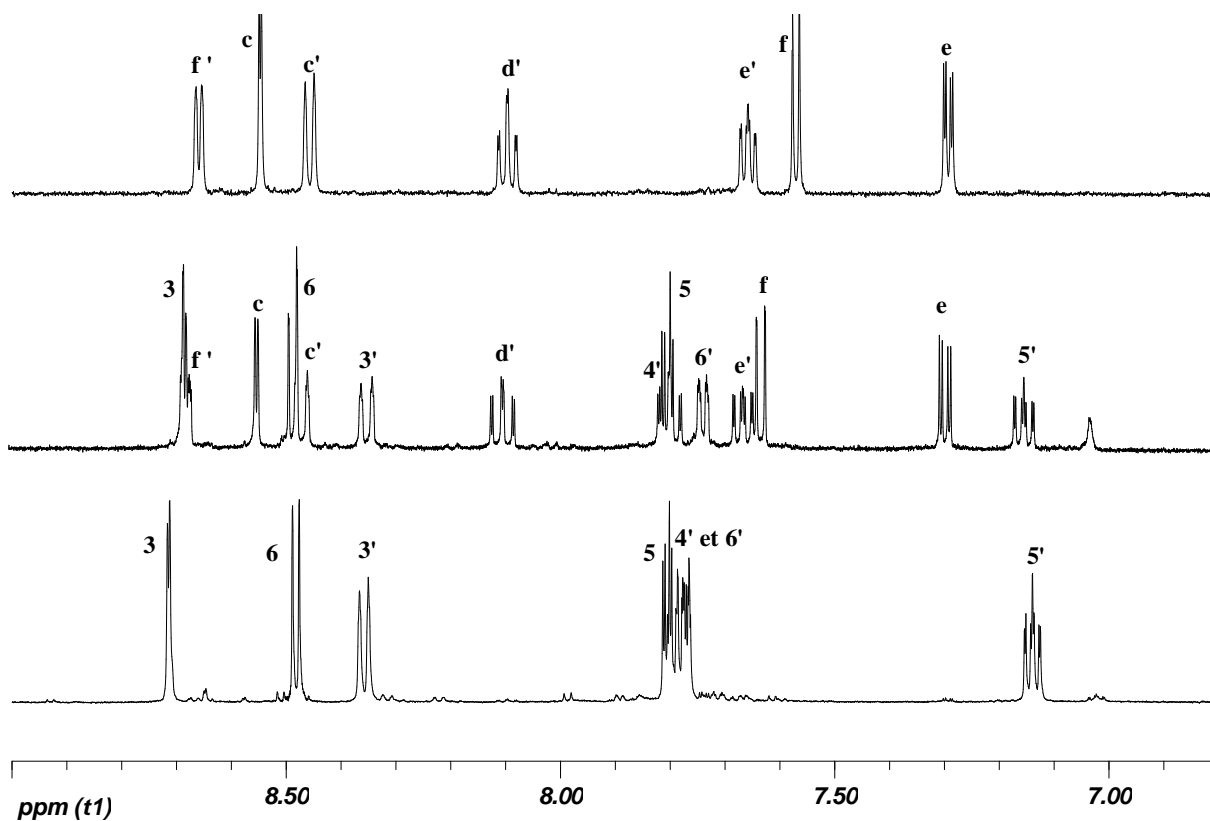
**Figure 2.** UV spectra (enlargement of the Figure 1) of complexes  $\text{Ru}(\text{bpy})_2\text{Cl}_2$ ,  $[\text{Ru}(\text{bpy})_2(\text{acac})](\text{PF}_6)$ ,  $[\text{Ru}(\text{bpy})_2(\text{tipsepd})](\text{PF}_6)$ , **1**, **2** and **3** in  $\text{CH}_2\text{Cl}_2$

Complexes **1**, **2** and **3** have three geometric isomers. In addition, they are chiral. Because of its low solubility, we were not able to separate the isomeric forms for **1** by HPLC technique, and then NMR data for **1** was untreatable because of its complexity (see supplementary materials, Figure S6). We did not pay too much attention to its separation due to the fact that **1** was considered as a reactional intermediate. However for **2** and **3**, we succeeded to separate them by HPLC on C18 column (see supplementary materials, Figure S4 and S5). The three isomers are shown on scheme 2. For the  $\alpha$  form, each substituent ( $\text{X}=\text{Br}$  or  $\text{X} = 2\text{-methyl-3-butyn-2-ol}$ ) of the pyridine ring are located in trans position to an oxygen atom of the acetylacetonato ligand. For the  $\beta$  form, only one substituent is located in trans position to an oxygen atom, the other is not. For the  $\gamma$  form, no substituents are located in trans position to oxygen atoms, so they are aligned. Only  $\alpha$  and  $\gamma$  isomers present a symmetry axis. From analytic HPLC experiment, (see Figure S4-S5) one can extract the relative proportion of each isomers:  $\alpha = 12\%$ ,  $\beta = 53\%$ ,  $\gamma = 35\%$  for complex **2** and  $\alpha = 9\%$ ,  $\beta = 48\%$ ,  $\gamma = 43\%$  for complex **3**.

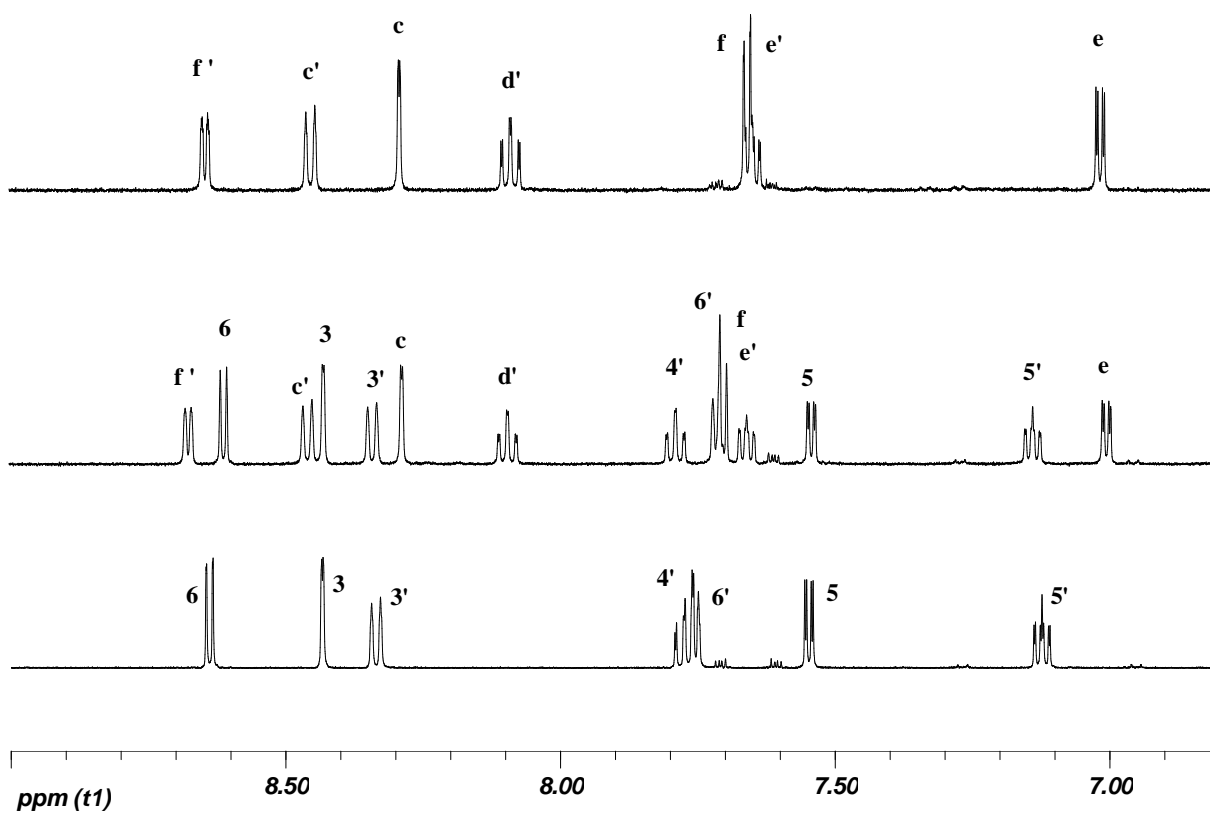


**Scheme 2.** Isomeric forms for complex **2** ( $\text{X} = \text{Br}$ ) and **3** ( $\text{X} = 2\text{-methyl-3-butyn-2-ol}$ )

NMR experiments have been made on the three unequivocal isomeric forms ( $\alpha$ ,  $\beta$ ,  $\gamma$ ) for **2** and **3**. The  $^1\text{H}$  NMR data (aromatic part) for complexes **2** and **3** are shown in Fig. 3 and 4 respectively (see also supplementary materials, Figure S7 and S8). In Both figures, the three forms are represented. All the  $^1\text{H}$  and  $^{13}\text{C}$  signals were unambiguously assigned on the basis of chemical shifts, spin-spin coupling constants, splitting patterns and signal intensities, and by using  $^1\text{H}$ - $^1\text{H}$  COSY and are presented on the reference section for complex **2** and complex **3**

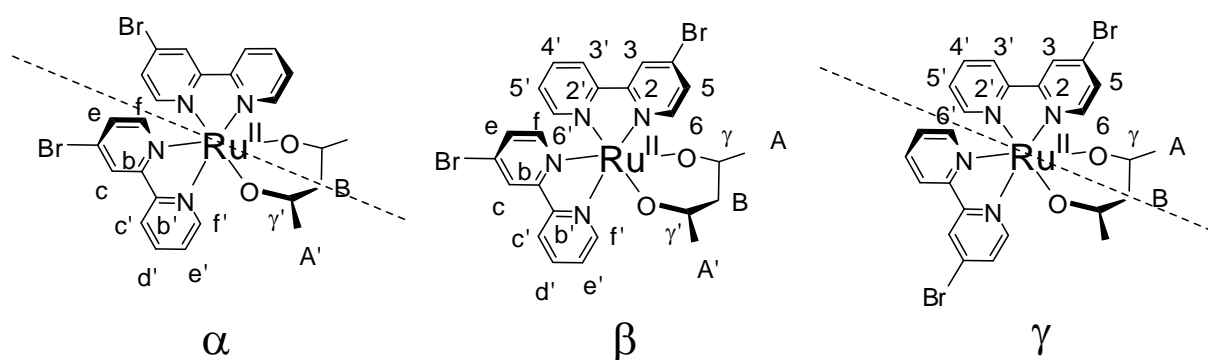


**Figure 3.**  $^1\text{H}$  NMR spectra (aromatic area) of complex **2**, top:  $\alpha$  form; middle:  $\beta$  form; bottom:  $\gamma$  form.



**Figure 4.**  $^1\text{H}$  NMR spectra (aromatic area) of complex **3**, top:  $\alpha$  form; middle:  $\beta$  form; bottom:  $\gamma$  form.

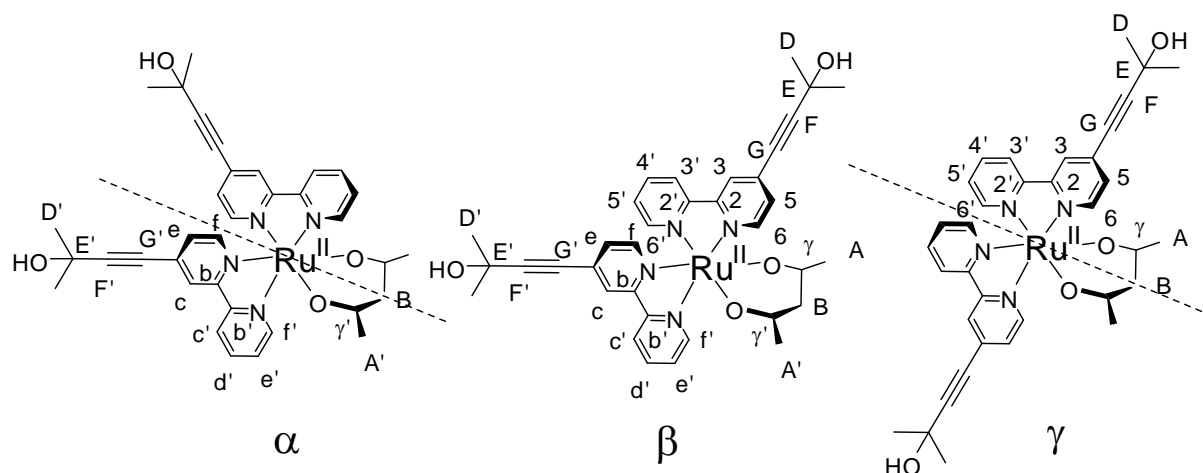
For complex **2**, (see scheme 3) it was quite easy to identify protons 3 and c with the J coupling (2 Hz). Thanks to NOESY experiment, spatial interaction were observed between c and c $\phi$  ( $\alpha$  form), 3 and 3 $\phi$  ( $\gamma$  form), as well as c, c $\phi$  and 3, 3 $\phi$  ( $\beta$  form).  $^1\text{H}$ - $^1\text{H}$  COSY experiment helped us to assign protons 5, 6 ( $\gamma$  form) and e, f ( $\alpha$  form). It has to be noted that the cycle current of the pyridine ring has strong influence on the protons located - on the brominated pyridine for the  $\alpha$  form (protons e, c and f) and - on the non-brominated pyridine for the  $\gamma$  form (protons 3 $\phi$  4 $\phi$  5 $\phi$  and 6 $\phi$ ).



**Scheme 3.** Isomeric forms of complex **2** with proton and carbon numbering for NMR assignments.

For the  $\gamma$  form, protons 5 (7.79 ppm) and 3 (8.71 ppm) located in ortho position in relation to the bromine atom are deshielded and proton 6 in meta position is slightly shielded. 6 $\phi$ (7.73ppm) is strongly shielded by the cycle current and this effect is less pronounced for 5 $\phi$  4 $\phi$  and 3 $\phi$  For the  $\alpha$  form, protons e (7.29 ppm) and c (8.55 ppm) are deshielded because of their ortho position towards bromine atom but less than 5 or 6 ( $\gamma$  form) because of the shielding current cycle effect. f (7.57 ppm) is strongly shielded because of the combined current cycle effect and of its meta position facing the bromine atom. If we compare **3** and **2**, (see scheme 4) one can note that the protons of the non-substituted pyridine do not significantly change ( $\Delta\delta_{\text{H}} < 0.02$  ppm), this is true for the three forms ( $\alpha$ ,  $\beta$ ,  $\gamma$ ). By substituting bromine by alkynyl group, the protons in ortho position are slightly shielded ( $\Delta\delta_{\text{H}} \sim 0.27$  ppm). In the same way, the proton f ( $\alpha$  form) and 6 ( $\gamma$  form) in meta position in regard to the substituent are slightly deshielded but differently:  $\Delta\delta_{\text{H}} \sim 0.08$  ppm for f and  $\Delta\delta_{\text{H}} \sim 0.16$

ppm for 6. This is due to the shielding effect of the current cycle which is effective for f and not for 6.



**Scheme 4.** Isomeric forms of complex **3** with proton and carbon numbering for NMR assignments.

In summary, some novel bromo or alkynyl-bipyridine complexes of ruthenium(II) have been synthesized and characterized. Thanks to HPLC, isomeric forms ( $\alpha$ ,  $\beta$ ,  $\gamma$ ) for complex **2** and **3** have been successfully separated. By NMR techniques, all the protons of all the isomeric forms were fully assigned. These materials will be used in the future in the synthesis of polymetallic assemblies with potential applications in the field of quantum computation. [17, 18] Further studies are clearly deserved to define fully the scope and limitation of this methodology.

### 3. Supplementary material

Mass spectra (FAB, DCM) of complexes **1**, **2** and **3**, HPLC spectra for complex **2** and **3**, full  $^1\text{H}$  NMR spectra of complexes **1**, **2** and **3**,

### Acknowledgements

The authors thank CNRS and the WPI MANA program for financial support, Chantal Zedde (Service commun de HPLC, laboratoire des IMRCP, Toulouse) for technical assistance with HPLC measurements.

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