

Whole Microwave Syntheses of Pyridylpyrazole and of Re and Ru Luminescent Pyridylpyrazole Complexes

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ABSTRACT

The synthesis of 3-(2pyridyl)pyrazole (pypzH) by conventional methods requires refluxing at high temperatures during more than 16 h, but this is reduced to two consecutive steps of 2 h at 100 °C, and of 10 min at 50 °C in a microwave (MW) assisted synthesis. Its coordination as chelating ligand to the "*fac*-Re^IBr(CO)₃" and "Ru^{II}(bipy)₂" fragments also occurs MW assisted in 5 or 10 min, respectively. A new MW assisted synthetic method is also described

for the synthesis of the starting material $[\text{Ru}(\text{bipy})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$. Both pypzH complexes are characterized by X-ray crystallography, and the study of their photophysical properties support their phosphorescence. The electrochemistry of the Ru complex indicates that electrochemical oxidation is followed by a chemical process.

1. Introduction

The luminescence of d^6 complexes of the type $\text{fac-}[\text{ReX}(\text{CO})_3(\text{diimine})]$ and $[\text{Ru}(\text{bipy})_2(\text{diimine})]^{2+}$ is associated to their long-lived triplet metal-to-ligand charge transfer ($^3\text{MLCT}$) excited state [1]. The study of their physical properties has led to develop many and diverse applications for these complexes [2], such as their behavior as biomolecular agents [3], their photocatalytic activity for the reduction of CO_2 [4], or their role as molecular switches [5] or as cation sensors [6]. The presence of an acidic hydrogen in the diimine ligand may give rise to particularly interesting proton-coupled electron transfer (PCET) processes [7], or, once deprotonated, might also afford fascinating polymetallic complexes or supramolecular assemblies [8].

One of the diimine ligands meeting these requirements is 3-(2-pyridyl)pyrazole (pypzH), and the coordination of pypzH or its substituted derivatives to $\text{Re}(\text{I})$ or $\text{Ru}(\text{II})$ complexes have been already described [9,10]. There are many reports of coordinated pypzH type ligands, either as bidentate chelate ligands in their neutral form (Fig. 1a) [11], either as bridging 3-(2-pyridyl)pyrazolate (pypz^-) after deprotonation and coordination to a second metallic center (Fig. 1b). In the latter case, there are many reports of homobimetallic complexes [12], whereas examples of heterobimetallic complexes are scarce (Fig. 1c) [13]. We have reported the first complexes where a pyridylpyrazolate is bridging to three metals (Fig. 1d) [9c].

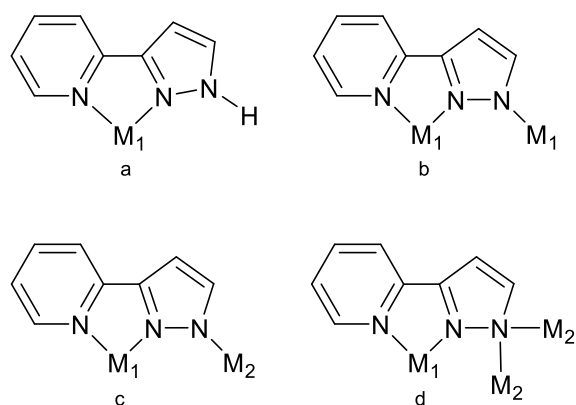
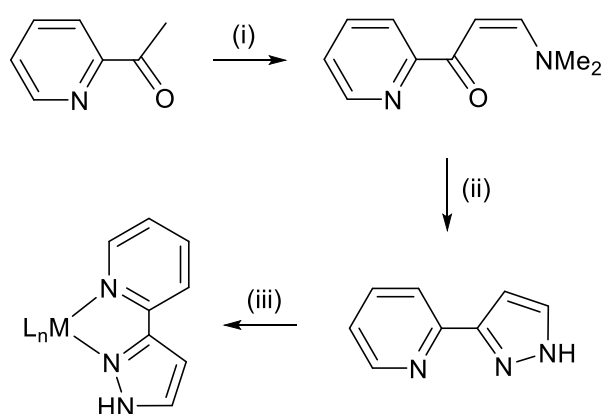


Figure 1. 3-(2-pyridyl)pyrazole and 3-(2-pyridyl)pyrazolate coordination modes.

The synthesis of the pypzH ligand or its substituted derivatives requires refluxing at high temperatures during more than 16 h, and their coordination to transition metals usually occurs by substitution of two weak or volatile ligands, such as NCMe or CO. This step may also require energetic conditions in order to favor the removal of the outgoing ligand(s). All these processes so far reported are usually achieved by using conventional heating. Herein we report the microwave (MW) syntheses of both the pypzH ligand, and of the luminescent complexes with the "*fac*-Re^IBr(CO)₃" and "Ru^{II}(bipy)₂" fragments. The use of MW for organic and organometallic synthesis is becoming an interesting alternative to conventional methods, because it lowers energy consumption, and enhances the selectivity, product purity, and yield [14]. There are many reports on the MW assisted syntheses of either organic molecules, either coordination complexes, but we are not aware of any previous report of a whole MW assisted syntheses of both the ligand and of its coordination to obtain transition metal complexes, as herein described.

2. Results and Discussion

Scheme 1 collects the reactions for synthesizing the pypzH ligand and its Re and Ru complexes. Herein, all these steps are carried out by MW assisted reactions. The synthesis of pypzH consists of a two-step process. Firstly 2-acetylpyridine and DMF-DMA react to obtain the dimethylamino substituted enone (Scheme 1, i). The reported conventional method requires a 2-fold excess of DMF-DMA, and refluxing at ca. 150°C for 16 h [15]. The same product is obtained in a MW reactor using the stoichiometric amount of DMF-DMA in only 2 h at 100°C (see Experimental Section). In the second step of the conventional synthesis (Scheme 1, ii), the enone previously obtained reacts in EtOH with N₂H₄·H₂O at 60°C during 30 min, to give the final pypzH [15]. The use of a MW reactor allows to reduce temperature and time to 50°C and 10 min, and the reaction is carried out solventless.



	conventional synthesis	MW synthesis
(i)	150 °C, 16 h, 2/1 excess, DMF-DMA	100 °C, 2 h, 1/1, DMF-DMA
(ii)	60 °C, 30 min, EtOH [15]	50 °C, 10 min, neat
(iii, Re) (1)	(1) 3 h, NCMc reflux; [16] (2) r.t. 1 h, CH ₂ Cl ₂ [9c]	200 °C, 5 min, hexane
(iii, Ru) (2)		150 °C, 10 min, H ₂ O

Scheme 1. Syntheses of pypzH and pypzH complexes (i) DMF-DMA; (ii) N₂H₄·H₂O; (iii) [ReBr(CO)₅] or [Ru(bipy)₂Cl₂]·2H₂O, NH₄PF₆ (ML_n = *fac*-Re^IBr(CO)₃, or *cis*-Ru^{II}(bipy)₂).

The coordination of pypzH to the appropriate Re(I) and Ru(II) fragments to obtain luminescent complexes is also depicted in Scheme 1, iii. The coordination to the *fac*-

$\text{Re}^{\text{I}}\text{Br}(\text{CO})_3$ fragment by conventional methods has been already described by us [9c], and requires two consecutive reactions to obtain *fac*-[ReBr(CO)₃(pypzH)] (**1**) from [ReBr(CO)₅]: firstly, the complex *fac*-[ReBr(CO)₃(NCMe)₂] is obtained after a 3 h reflux in MeCN [16], and then MeCN are substituted by pypzH after 1 h at room temperature in CH₂Cl₂ [9c]. Instead, the MW assisted reaction requires only one step from [ReBr(CO)₅], since complex **1** is readily obtained at 200°C after 5 min, in hexane. The reactions of [ReX(CO)₅] (X = halogen) with chelating ligands to afford the corresponding *fac*-Re^IX(CO)₃ complexes may be carried out also in one step by conventional heating, but usually require longer reflux periods. Finally, the ruthenium(II) complex [Ru(bipy)₂(pypzH)](PF₆)₂ (**2**) is herein described for the first time, and can be prepared in a MW reactor by treating [Ru(bipy)₂Cl₂] \cdot 2H₂O with the equimolar amount of pypzH and two equivalents of NH₄PF₆ at 150°C during 10 min in H₂O as solvent (see Experimental Section). A new MW assisted synthetic method is also herein described to synthesize the starting material [Ru(bipy)₂Cl₂] \cdot 2H₂O, reducing the reaction time from 8 h in refluxing DMF, as described for the conventional synthesis [17], to 1 h at 150°C in CHCl₃ (see Experimental Section). An additional advantage of this MW method is that the three reactions shown in Scheme 1 can be carried out consecutively in the same MW vial.

Both pypzH complexes have been characterized crystallographically. The crystal structures and selected distances and angles are depicted in Figures 2 and 3. As expected, both metals show a octahedral coordination and the distances and angles are similar to those found in other pypzH complexes [11]. In both structures the N-bound hydrogen of the pypzH ligand is involved in hydrogen bonding with molecules of solvent present in the crystals: with the oxygen atom of Et₂O (H3 \cdots O90 1.874(8) Å, N3 \cdots O90 2.731(7) Å, N3–H3 \cdots O90 174.8(4)°) in **1**, or with the nitrogen atom of NCMe (H7 \cdots N91 2.062(7) Å, N7 \cdots N91 2.898(7) Å, N7–H7 \cdots N91 164.1(3)°) in **2**. These distances and angles are in accordance with "moderate" hydrogen bonds [18].

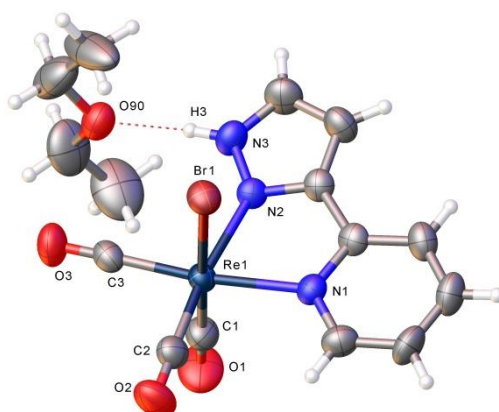


Figure 2. Perspective view of **1**·Et₂O showing the atom numbering. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (°): Re1-Br1 2.6275(5), Re1-N2 2.155(4), Re1-N1 2.204(4), Re1-C3 1.925(6), Re1-C1 1.904(6), Re1-C2 1.889(6), N2-Re1-Br1 83.51(10), N2-Re1-N1-73.40(15), N1-Re1-Br1 84.61(10), C3-Re1-Br1 91.69(15), C3-Re1-N2 100.75(19), C3-Re1-N1 173.37(18), C1-Re1-Br1 178.12(19), C1-Re1-N2 94.6(2), C1-Re1-N1 94.95(19), C1-Re1-C3 88.6(2), C2-Re1-Br1 91.69(17), C2-Re1-N2 169.60(19), C2-Re1-N1 97.0(2), C2-Re1-C3 88.6(2), C2-Re1-C1 90.2(2).

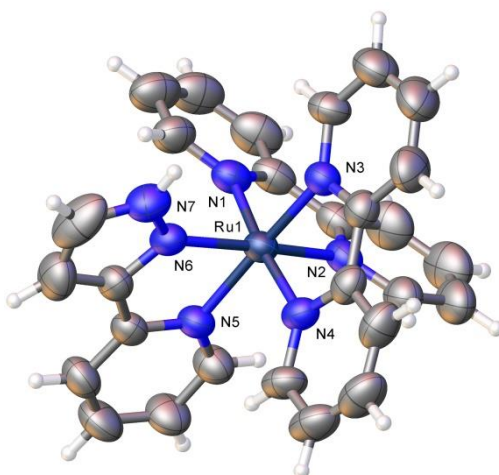


Figure 3. Perspective view of **2**·2MeCN showing the atom numbering (PF₆⁻ and MeCN are omitted for clarity). Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (°): Ru1-N1 2.062(3), Ru1-N2 2.058(3), Ru1-N3 2.064(3), Ru1-N4 2.055(3), Ru1-N5 2.079(3), Ru1-N6 2.065(3), N1-Ru1-N3 98.13(12), N1-Ru1-N5 87.89(12), N1-Ru1-N6 96.84(13), N2-Ru1-N1 78.64(13), N2-Ru1-N3 88.42(12), N2-Ru1-N5 95.77(12), N2-Ru1-N6 172.39(12), N3-Ru1-N5 173.26(12), N3-Ru1-N6 98.34(12), N4-Ru1-N1 174.06(12), N4-Ru1-N2 96.31(12), N4-Ru1-N3 78.48(12), N4-Ru1-N5 95.77(12), N4-Ru1-N6 88.52(12), N6-Ru1-N5 77.84(12).

The absorption and emission spectral data collected for both pypzH complexes are summarized in Table 1. Figure 4 shows representative absorption and emission spectra of **1** and **2**. The spectra show absorption profiles similar to previously reported complexes [9a-b,10b,19,20], and do not show significant changes in different solvents. Thus, the maximum

of the absorption spectrum for **1** in CHCl₃ (352 nm) may be attributed to a $d\pi(\text{Re})\rightarrow\pi^*(\text{L})$ MLCT band, whereas the weaker (271 nm) corresponds to $\pi(\text{L})\rightarrow\pi^*(\text{L})$ ILT [9a-b,19]. Similarly, the maximum displayed by the absorption spectrum of **2** in THF (445 nm) is attributed to a $d\pi(\text{Ru})\rightarrow\pi^*(\text{L})$ MLCT band, and the high-energy absorption band (287 nm) may be ascribed to $\pi(\text{L})\rightarrow\pi^*(\text{L})$ ILT [10b,20].

Table 1. Absorption and emission data of pypzH complexes in deaerated solvents and in optically dilute solutions, at 298 K.

	Absorption	Emission				
	λ (nm) ($\epsilon \times 10^{-3} \text{ M}^{-1}\text{cm}^{-1}$)	λ_{em} (nm)	$\Phi \times 10^{-2}$ ^(c)	τ (ns)	$k_{\text{r}} \times 10^4 \text{ s}^{-1}$	$k_{\text{nr}} \times 10^4 \text{ s}^{-1}$
1 ^a	271 (25.0), 352 (2.5)	519	5.0	188.2	26.5	504.9
2 ^b	236 (29.0), 287 (54.9), 373 (8.2), 414 (9.7), 445 (10.1)	645	1.7	174.0	9.9	564.7

^aCHCl₃, [$\lambda_{\text{excit}} = 360 \text{ nm}$]. ^bTHF, [$\lambda_{\text{excit}} = 420 \text{ nm}$]. ^c $\pm 8\%$. Absolute luminescence quantum yield values are measured using the integrating sphere accessory,

The emission spectra of both complexes show one unstructured broad band, which is solvent-dependent, due to a light hypsochromic effect (519 or 645 nm in THF for **1**, and 515 or 629 nm in the more polar MeCN for **2**). The intensities in the emission spectra of both complexes show a dramatic increase in deaerated solutions compared to those prepared without exclusion of air, with no variation in the emission maxima (see Figure S1 and Table S1 in Supplementary Material). These results, along with luminescent emission lifetimes (see below), are characteristic features of ³MLCT phosphorescent emissions [21].

The quantum yield of **1** (0.05) is also slightly higher than those reported for other pypzR rhenium(I) complexes [9a-b], which are also higher than those of rhenium bipy and phen complexes [19b-d]. The quantum yield of **2** (0.017) is higher than those reported for other pyridylpyrazole ruthenium(II) complexes [20c], although lower than those reported for bipy and phen ruthenium complexes [20,22].

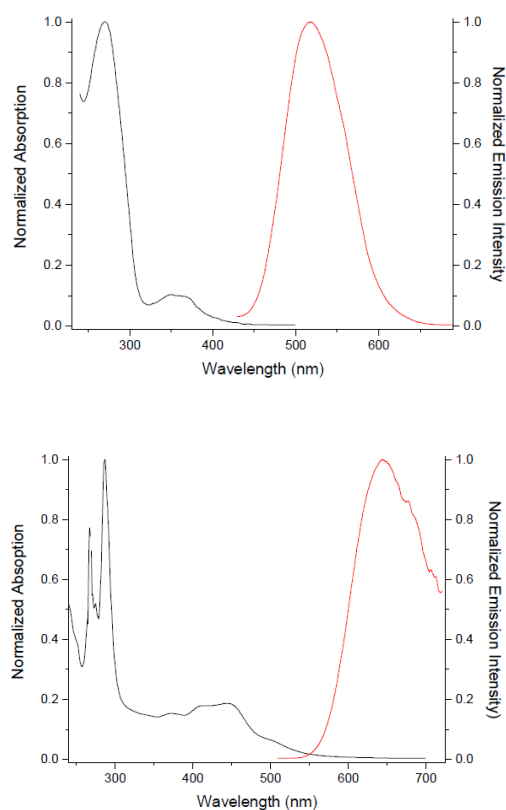


Figure 4. Normalized UV/vis absorption (black) and emission (red) spectra of complexes **1** (above, CHCl_3 , [$\lambda_{\text{excit}} = 360 \text{ nm}$]), and of **2** (below, THF, [$\lambda_{\text{excit}} = 420 \text{ nm}$].) at 298 K, in deaerated solvents and in optically dilute solutions.

Finally, the luminescent emission lifetimes are in the range of those previously reported for similar Re and Ru complexes [10b,19c,d,20b,22b], whereas radiative decay rate constant (k_r) values are slightly higher [19b-d,20b,22b]. This parameter is an indication of the efficiency in the luminescent emission processes, what points to promising results in future works on this type of complexes.

The redox properties of **1** have been previously described [9c], and the electrochemistry of the complex **2** is herein reported. As depicted in Figure 5, the cyclic voltammetry study reveals to be strongly dependent on the scan rate. The collected curves under different experimental conditions (scan rates, initial, vertex and final potentials) are included in the Supplementary Material.

Cyclic scans initiated by oxidations from 0 V \rightarrow +1.8 V \rightarrow 0 V (Figure 5) show that the electron transfer Ru(II) \rightarrow Ru(III), with $E_{1/2}$ at +1.26 V, is chemically irreversible ($i_c/i_a > 1$). The electron transfer is also electrochemically irreversible, with ΔE values going from 190 mV at 20 mV s⁻¹ to 630 mV at 1000 mV/s, and far from diffusion controlled conditions (i.e. i_a/\sqrt{v} not constant). The half-wave potential observed for the couple Ru(III)/Ru(II) at +1.26 V is similar to that found for [Ru(bipy)₃]²⁺ (1.29 V in MeCN) [23]. The related complexes [Ru(bpy)₂(pyridine-arylimine)]²⁺ also exhibit reduction potentials in the range 1.46 to 1.51 V in CH₂Cl₂ depending on the aryl substituents [24].

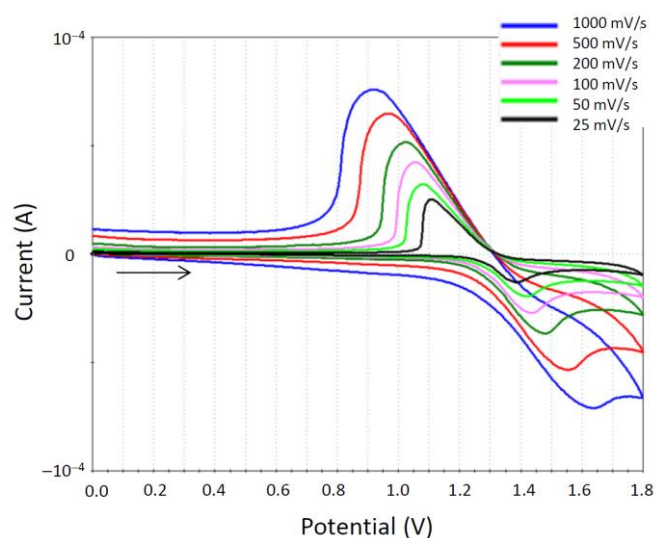


Figure 5. Cyclic voltammograms recorded in 1.5 mM CH₂Cl₂ solutions of **2** at different scan rates (from 20 to 1000 mV s⁻¹).

Cyclic scans initiated to reductions from 0 V \rightarrow -1.8 V \rightarrow 0 V (see Supplementary Material) show a monoelectronic reduction with $E_{1/2} = -1.57$ V, which may be assigned to a ligand centered electron transfer. Scanning to such negative potentials strongly perturbs the following scans to positive potentials. In fact, a new wave emerges at $E_{1/2} = +0.76$ V (see Supplementary Material), that was absent in the first scan to positive potentials with a new electrode. Furthermore, scanning to negative potentials pollutes the electrode, leading to

erratic measurements on the cathodic and anodic currents of the wave centered at +1.26 V (see Supplementary Material). Nevertheless, the electrode becomes clean after reaching +1.6 V in the scan. Consequently, repetitive results may be only obtained by doing separate scans from 0 V to positive potentials or to negative potentials, but not by doing full cyclic scans around the complete window of the solvent.

The observed electrochemical behavior may be understood by accepting that complex **2** (abbreviated as $[2]^{2+}$) undergoes an E_1CE_2 mechanism [25]. The first electrochemical step E_1 corresponds to $[2]^{2+} - e^- \xrightarrow{E_1} [2]^{3+}$, with a mean estimated value of $E_{1/2} = +1.26V$, calculated as $E_{1/2} = \frac{E_{ox} + E_{red}}{2}$, which is approximately constant for the different scan rates (see Figure 5). To this electron transfer follows up a chemical reaction that accounts for the anomalous observed behavior. The kinetics of the chemical reaction control the appearance of the cyclic voltammograms under different scan rates.

Finally, in order to understand why $i_c/i_a > 1$, we may think that the anodic current i_a is fed only by diffusion, while the cathodic current i_c is fed both by diffusion and by the chemical reaction that follows the oxidation.

3. Conclusions

MW assisted synthesis allows to obtain both the pypzH ligand and luminescent Re and Ru complexes containing this ligand in mild conditions, when compared to those previously reported by conventional methods. The complex $[Ru(bipy)_2(pypzH)](PF_6)_2$ (**2**) is herein described for the first time. Both pypzH complexes are phosphorescent, and display radiative decay rate constant values slightly higher than those for similar complexes previously described, what points to a higher efficiency in the luminescent emission processes. The electrochemistry of the Ru complex shows that the electrochemical oxidation is followed by a

chemical process. These results open an interesting alternative to conventional synthetic methods, given the promising photophysical and electrochemical properties of these complexes.

3. Experimental Section

3.1. General Remarks

For conventional reactions, all manipulations were performed under N₂ atmosphere following conventional Schlenk techniques. For microwave assisted reactions, all manipulations were carried out without exclusion of air. Solvents were purified according to standard procedures. [ReBr(CO)₅] [26], and [RuCl₂(dmsO)₄] [27] were synthesized as previously described, and the rest of reagents were obtained from the usual commercial suppliers, and used as received.

Microwave reactions were carried out in 4 or 10 mL vial receptacles on a Anton Paar Monowave 300. Infrared spectra were recorded in Bruker Tensor 27 FTIR spectrometer. NMR spectra were recorded in a MR 400 or 500 DD2 Agilent instruments at room temperature (r.t.), and the chemical shifts are referred to the internal residual solvent peak both for ¹H and ¹³C{¹H} NMR. Assignment of the ¹H NMR spectra (Figure 6) was supported by COSY, TOCSY and NOESY experiments, and assignment of ¹³C{¹H} NMR data was supported by HMBC and HSQC heteronuclear experiments. Elemental analyses were performed on a Thermo Fisher Scientific EA Flash 200.

3.2. [Ru(bipy)₂Cl₂]**·**2H₂O

Its synthesis by conventional methods and some spectroscopic data have been previously reported [17]. **MW assisted method:** A mixture of [RuCl₂(dmsO)₄] (0.200 g, 0.41 mmol), bipy (0.128 g, 0.82 mmol) and CHCl₃ (3 mL) was heated in a microwave oven for 1 h at 150

°C. The black solid obtained was filtered off and washed thoroughly with water (5 × 20 mL), and then with Et₂O (2 × 10 mL), and vacuum dried. Yield: 0.166 g (78%). IR (cm⁻¹): 3664 m br, 3469 w, 3101 w, 3070 w, 3031 w, 2638 w, 2324 w, 2238 w, 2164 w, 1981 w, 1876 w, 1670 w, 1613 m, 1600 m, 1562 w, 1479 w, 1460 m, 1442 s, 1417 s, 1320 w, 1308 m, 1265 m, 1243 w, 1156 w, 1122 w, 1106 w, 1065 w, 1036 m, 1018 w, 976 w, 963 w, 902 w, 886 w, 799 m, 763 vs, 728 s, 656 m, 645 w. ¹H NMR (500 MHz, CD₃CN) δ 10.08 (s, H⁶, 2 H), 8.39 (d, J = 8.2 Hz, H³, 2 H), 8.24 (dd, J = 8.1, 1.4 Hz, H^{3'}, 2 H), 8.01 (td, J = 7.8 and 1.4 Hz, H⁴, 2 H), 7.69 (t, J = 6.5 Hz, H⁵, 2 H), 7.66–7.55 (m, H^{4'} and H^{6'}, 4 H), 7.02 (t, J = 6.4 Hz, H^{5'}, 2 H). ¹³C{¹H} NMR (126 MHz, CD₃CN): 160.89 (C^{2'}), 158.83 (C²), 153.58 (C⁶), 152.77 (C^{6'}), 134.68 (C⁴), 133.50 (C^{4'}), 125.37 (C⁵), 125.01 (C^{5'}), 122.60 (C^{3'}), 122.24 (C³).

3.3. 3-(2-Pyridyl)pyrazole (pypzH)

Its synthesis by conventional methods and some spectroscopic data have been previously reported [15a,b]. **MW assisted method:** A mixture of 2-acetylpyridine (0.22 mL, 2 mmol) and DMF-dimethylacetal (0.27 mL, 2 mmol) was heated in a microwave oven for 2 h at 100 °C, and then the volatiles were removed in vacuo. The brown red solid was mixed with hydrazine hydrate (0.2 mL, 4 mmol) and heated in a microwave oven for 10 min at 50 °C. The volatiles were removed in vacuo, the red residue was washed with water (3 × 5 mL), and the ochre solid thus obtained was dried in vacuo, and recrystallized from CH₂Cl₂/hexane, yielding 0.19 g (65%). IR (cm⁻¹): 3124 m, 3058 m, 3023 m, 2978 m, 2937 m, 2898 m, 2835 m, 2802 m, 2735 m, 2654 w, 2501 w, 2324 w, 2165 w, 2051 w, 1981 w, 1704 w, 1590 s, 1567 m, 1536 w, 1502 m, 1454 m, 1416 s, 1357 m, 1303 m, 1271 w, 1231 m, 1192 w, 1144 m, 1129 w, 1088 m, 1059 m, 1048 m, 1036 w, 1000 w, 993 m, 950 m, 924 w, 877 m, 843 m, 797 m, 757 vs, 704 s, 695 m, 627 m, 615 m. ¹H NMR (400 MHz, CDCl₃) δ 11.70 (s, NH, 1 H), 8.63 (dt, J = 4.9 and 1.2 Hz, H³, 1 H), 7.73 (dt, J = 8.2 and 4.1 Hz, H⁶ and H⁴, 2 H), 7.64 (d, J

= 2.1 Hz, H^4 , 1 H), 7.22 (dd, $J = 8.1, 4.9$ Hz, $H^{5'}$, 1 H), 6.77 (s, H^5 , 1 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 206.95 ($C^{2'}$), 192.18 (C^3), 149.43 ($C^{3'}$), 136.45 ($C^{4'}$ and C^4), 122.80 ($C^{5'}$), 120.03 ($C^{6'}$), 103.32 (C^5).

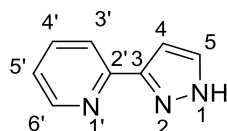


Figure 6. Numbering of pypzH for NMR assignment.

3.4. *fac*-[ReBr(CO)₃(pypzH)]

Its synthesis by conventional methods and complete spectroscopic data have been previously reported [9c]. **MW assisted method:** A mixture of [ReBr(CO)₅] (0.041 g, 0.1 mmol), pypzH (0.015 g, 0.1 mmol), and hexane (2 mL) was heated in a microwave oven for 5 min at 200 °C. The solvent was removed and dried in vacuo and the pale yellow solid obtained was spectroscopically pure. Analytical data were consistent with those reported previously.

3.5. [Ru(bipy)₂(pypzH)](PF₆)₂

MW assisted method: A mixture of [Ru(bipy)₂Cl₂] \cdot 2H₂O (0.052 g, 0.1 mmol), pypzH (0.015 g, 0.1 mmol), NH₄PF₆ (0.033 g, 0.2 mmol), and H₂O (0.5 mL) was heated in a microwave oven for 10 min at 150 °C. The orange solid obtained was filtered off and washed thoroughly with water (5 \times 5 mL), and then with Et₂O (2 \times 5 mL), and vacuum dried. Yield: 0.070 g (82%). IR (cm^{-1}): 3656 w, 3364 m, 3115 w, 2164 w, 2051 w, 1981 w, 1606 w, 1568 w, 1516 w, 1464 m, 1447 m, 1377 w, 1313 w, 1270 w, 1244 w, 1164 w, 1126 w, 1111 w, 1090 w, 1070 w, 1028 w, 975 w, 929 w, 893 w, 880 w, 827 vs, 756 vs, 729 s, 660 m, 649 m, 612 w. ^1H NMR (500MHz, $\text{Me}_2\text{CO}-d^6$): 7.43 (ddd, $J = 7.7, 5.7,$ and 1.5 Hz, $H^{5'}$ pypzH, 1 H), 7.50 (ddd, $J = 7.7, 5.6,$ and 1.3 Hz, H^5 bipy¹, 1H), 7.54 (d, $J = 2.9$ Hz, H^4 pypzH, 1 H), 7.57 (ddd, J

= 7.7, 5.6, and 1.4 Hz, $H^{5'}$ bipy², 1 H), 7.61 (ddd, J = 7.7, 5.7, and 1.4 Hz, H^5 bipy², 1 H), 7.64 (ddd, J = 7.7, 5.6, and 1.4 Hz, $H^{5'}$ bipy¹, 1 H), 7.89 (ddd, J = 5.7, 1.5, and 0.8 Hz, $H^{4'}$ pypzH, 1 H), 8.01 (ddd, J = 5.6, 1.5, and 0.7 Hz, $H^{4'}$ bipy¹, 1 H), 8.03-8.07 (m, H^4 bipy¹ and H^4 bipy², 2 H), 8.11 (ddd, J = 5.7, 1.5, and 0.7 Hz, H^4 bipy², 1 H), 8.15 (d, J = 2.9 Hz, H^5 pypzH, 1 H), 8.11-8.17 (m, $H^{6'}$ pypzH and H^6 bipy¹, 2 H), 8.17-8.25 (m, H^6 and $H^{6'}$ bipy², and H^6 bipy¹, 3 H), 8.47 (ddd, J = 8.0, 1.5, and 0.8 Hz, $H^{3'}$ pypzH, 1 H), 8.75 (ddd, J = 8.2, 1.3, and 0.7 Hz, H^3 bipy¹, 1 H), 8.78-8.82 (m, H^3 and $H^{3'}$ bipy², and $H^{3'}$ bipy¹, 3 H), 13.52 (s, NH pypzH, 1 H). ¹³C{¹H} NMR (126 MHz, Me₂CO-*d*⁶): 105.6 (C⁴ pypzH), 123.0 (C^{3'} pypzH), 123.9 (C^{3'} bipy²), 124.0 (C³ bipy¹), 124.3 (C^{3'} bipy¹), 124.4 (C³ bipy²), 125.7 (C^{5'} pypzH), 127.3 (C⁵ bipy¹), 127.7 (C⁵ bipy²), 127.8 (C^{5'} bipy²), 127.9 (C^{5'} bipy¹), 134.8 (C⁵ pypzH), 137.7 (C⁶ bipy¹), 137.8 (C^{6'} bipy¹), 138.0 (C^{6'} bipy²), 138.2 (C⁶ bipy²), 151.7 (C^{4'} pypzH), 151.8 (C³ pypzH), 152.0 (C^{4'} bipy²), 152.0 (C⁴ bipy²), 152.3 (C^{4'} bipy¹), 152.5 (C⁴ bipy¹), 153.4 (C^{2'} pypzH), 157.3 (C^{2'} bipy¹), 157.6 (C^{3'} bipy¹), 157.9 (C² bipy¹), 157.9 (C^{2'} bipy²). Anal. Calcd for C₂₈H₂₃F₁₂N₇P₂Ru: C, 39.63; H, 2.73; N, 11.56. Found: C, 39.70; H, 2.67; N, 11.64.

3.6. Crystal Structure Determination for Compounds 1·Et₂O and 2·2MeCN.

Crystals were grown by slow diffusion of Et₂O into concentrated solutions of the complexes in acetone (for *fac*-[ReBr(CO)₃(pypzH)]) or MeCN (for [Ru(bipy)₂(pypzH)](PF₆)₂) at -20 °C. Relevant crystallographic details can be found in the CIF. A crystal was attached to a glass fiber and transferred to an Agilent SuperNova diffractometer fitted with an Atlas CCD detector. The crystals were kept at 293(2) K during data collection. Using Olex2 [28] the structure was solved for the Re complex with the ShelXT structure solution program using direct methods [29], and with olex2.solve structure solution program using Charge Flipping for the Ru complex [28], and then, the structures were refined with the ShelXL refinement

program using least squares minimisation [29]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. All graphics were made with Olex2, and distances and angles of hydrogen bonds were calculated with PARST [30] (normalized values) [31]. Compound **1** crystallized with one molecule of ethyl ether, while compound **2** crystallized with two molecules of acetonitrile. One of the acetonitrile molecules is disordered over two positions (being 0.67 the percentage of the major component), and had to be refined with DFIX, DELU and SAME restraints to obtain a chemically reasonable model.

3.7. Photophysical studies

The solvents for spectroscopic studies were of spectroscopic grade and used as received. Ultraviolet–visible (UV-Vis) and fluorescence spectra were recorded in optically dilute solutions (from 10^{-5} M to 5×10^{-5} M), at room temperature with a quartz cuvette (1 cm \times 1 cm), using a Hitachi U-3900 and an F-7000 Hitachi Fluorescence spectrophotometers, respectively. Fluorescence decay lifetimes were measured in deaerated solvents, using a time-correlated single photon counting instrument (FLS980 Series, Edinburgh instruments) with a 405 nm pulsed LED (Edinburgh instruments, EPL-510) light source having a 50-500 ns. The absolute fluorescence quantum yields in each solvent were measured using the integrating sphere accessory with a FLS980 Series Edinburgh instrument, wherein the solvent was used as a reference.

3.8. Electrochemical experiments

Electrochemical experiments were carried out in a one-cavity three-electrode cell, using platinum disk working electrode ($\phi = 3$ mm), platinum wire counter electrode ($\phi = 0.5$ mm), and SCE as reference electrode in dichloromethane. All the potentials reported are referred to

standard saturated calomel electrode (SCE). The redox properties of complex [Ru(bipy)₂(pypzH)](PF₆)₂ were analyzed by means of cyclic voltammetry (CV) in a solution 0.1 M of (ⁿBu₄N)(PF₆) (TBAH) in CH₂Cl₂, and their redox potentials are referred to the SCE electrode. CVs were run at different scan rates. After each measurement the reference was checked against the E^o ferrocene–ferricinium couple as an internal calibrant (+0.47 V against the SCE reference electrode in CH₂Cl₂ solution under the conditions described above).

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