

Unusual phenomenon in the chemistry of orthometalated ruthenium (II) complexes

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Abstract

Yellow cyclometalated ruthenium (II) complexes $[\text{Ru}(o\text{-X-2-py})(\text{MeCN})_4]\text{PF}_6$ (**1**, X = C₆H₄ (**a**) or 4-MeC₆H₃ (**b**)) react readily with 1,10-phenanthroline (LL) in MeCN to give brownish-red species *cis*- $[\text{Ru}(o\text{-X-2-py})(\text{LL})(\text{MeCN})_2]\text{PF}_6$ in high yields. The same reaction of the same complexes under the same conditions with 2,2'-bipyridine results in a significant color change from yellow to brownish-orange suggesting a formation of new species. Surprisingly, X-ray structural studies of these two complexes showed that they are structurally indistinguishable from the starting complexes **1**. Referred to as complexes **4a,b**, the new compounds are slightly more stable in the air though their spectral characteristics in solution are similar to **1a,b**. The diffuse reflectance spectroscopy is so far the only technique that indicated differences between **1** and **4**.

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1. Introduction

This communication has appeared in the Topical issue of Inorganica Chimica Acta because of an extreme tolerance of the reviewers. The limits of modern peer-review guiding principles accepted nowadays by comprehensive leading chemical journals make it extremely difficult, perhaps just impossible, to report the data which are unusually curious and challenging but cannot be completely understood and explained at a moment. If similar practice has prevailed previously, the inorganic community would have learned about the Zeise salt in

1954, when its X-ray structural characterization has been reported, not in 1825, when the compound has actually been described [1]. In this communication we wish to share with those who are particularly interested in Ru and Os chemistry our recent mysterious observations related to the chemistry of orthometalated Ru^{II} derivatives of 2-phenylpyridine and 2-(4-tolyl)pyridine $[\text{Ru}(\text{C-N})(\text{MeCN})_4]\text{PF}_6$ (**1a** and **1b**, respectively). Recently, we have reported that yellow complexes **1** react with 1,10-phenanthroline (phen) in acetonitrile to form complexes **2a,b** in good yields. The synthesis of similar 2,2'-bipyridine (bpy) complexes **3a,b** is more tricky and laborious; methylene chloride should be used as a solvent [2]. It has been previously only mentioned about **1** and bpy that “when 2,2'-bipyridine reacts with **1a** or

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1b in MeCN under identical conditions, the solutions turn brown; new brownish-orange crystalline materials (here **4a** and **4b**) have been isolated in both cases. The composition of both products appears to be identical to that of **1a** and **1b**. These facts are currently under intensive investigation” [2]. Here we report the experimental details on interaction of complexes **1a** or **1b** with bpy in MeCN. Our studies showed that phen substitutes readily two *cis*-MeCN ligands at Ru^{II} in MeCN, whereas bpy cannot be coordinated to the Ru^{II} center under similar conditions. Instead, 2,2'-bipyridine and pyridine change strongly the color of complexes **1** from yellow to brownish-orange, make them more stable in the air, but the X-ray structural characterization of these isolated complexes **4a** and **4b** has revealed that they are structurally indistinguishable from starting materials **1a** and **1b** (see Scheme 1).

2. Results and discussion

2.1. General comments and observations

Complexes **1a,b** have been made from 2-phenylpyridine (C₆H₅-2-py) or 2-(4-tolyl)pyridine (MeC₆H₄-2-py) and [(η⁶-C₆H₆)RuCl(μ-Cl)]₂ [3]. Lemon-yellow solid materials **1a** and **1b** are unstable in the air and turn gradually yellowish green and then dark green [2,3]. Nevertheless they are convertible into brownish-red species [Ru(*o*-C₆H₄-2-py)(LL)₂](PF₆) (LL = bpy or phen) in MeOH as solvent [4]. Similar reaction at a 1:1 stoichiometry between **1a,b** and phen in MeCN affords brownish-red complexes **2a,b**. Their bpy counterparts **3a,b** are not formed in the MeCN but could be prepared in CH₂Cl₂ as solvent [2]. The reactions of complexes **1a** and **1b** with bpy instead of phen in MeCN under absolutely identical conditions resulted in a color change and “new” brownish-orange crystalline materials **4a** and **4b**, respectively, more stable both in the air and

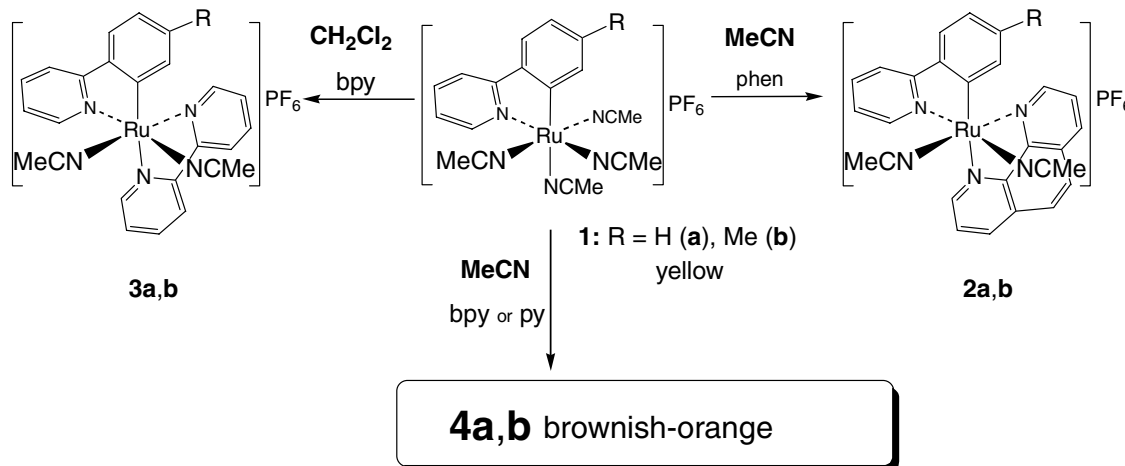


Fig. 1. Photographs of complexes **1a** and **4a**. Note a yellow color of **1a** and a brownish-orange color of **4a**. Similar difference is observed for **1b** and **4b** (see Fig. 2).

solution, were isolated in both cases. The conversion of **1b** into the brownish-orange complex **4b** is a bit slower than the conversion of **1a**. Under the irradiation by a 200 W bulb lamp, the **1a** → **4a** conversion in MeCN in the presence of 1 equiv. bpy is complete in a matter of 1.5–2 h at 20 °C. When the reaction is incomplete, a mixture of yellow and brownish-orange crystals is obtained on crystallization using a slow diffusion technique. However, it is not possible to separate the yellow species from the brownish-orange one by column chromatography. The same photochemical acceleration though less pronounced has also been observed for complex **1b**. The color of complexes **1** and **4** vary so strikingly (Fig. 1) that there has been no doubt that **1** and **4** are different compounds. Surprisingly, the X-ray crystal structures (Fig. 2) of **1** and **4** are identical.

2.2. X-ray structural characterization of complexes **4a** and **4b**

In order to identify dissimilarities between yellow species **1a,b** and brownish-orange complexes **4a,b**, crystals of **4a** and **4b** suitable for X-ray crystallographic studies have



Scheme 1.

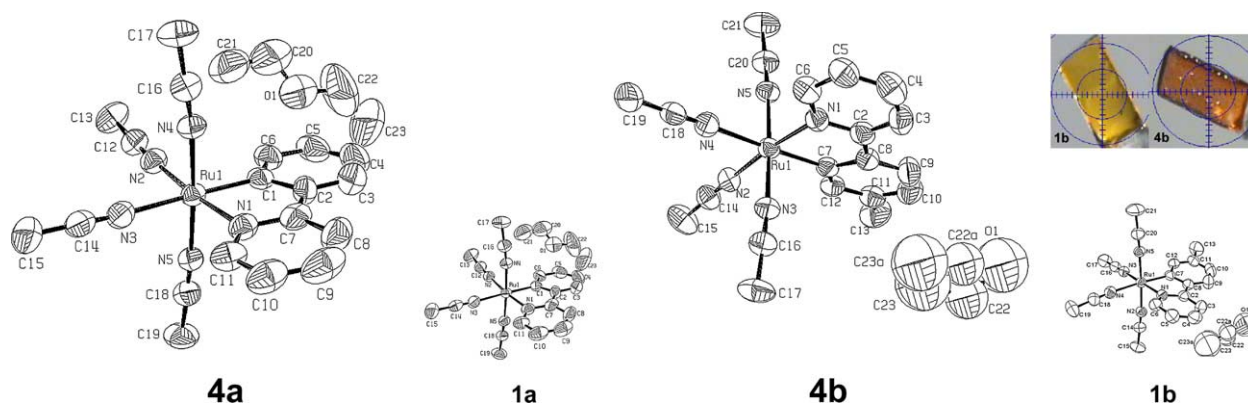


Fig. 2. ORTEP diagrams for cationic complexes **4a** and **4b** (H atoms and the PF_6^- counter ion are not shown for clarity). Ellipsoids represent a 50% probability level. Previously published [2] structures of **1a** and **1b** are shown for comparison. Selected bond lengths for **4a** [**1a** for comparison]: Ru–C1 2.014(6) [2.014(6)], Ru–N1 2.049(5) [2.051(5)], Ru–N2 2.048(5) [2.055(6)], Ru–N3 2.147(5) [2.154(6)], Ru–N4 2.010(4) [2.019(5)], and Ru–N5 2.003(5) [2.015(5)] Å. Selected bond lengths for complex **4b** [**1b** for comparison]: Ru–C7 2.021(5) [2.024(5)], Ru–N1 2.060(4) [2.009(4)], Ru–N2 2.033(4) [2.021(4)], Ru–N3 2.018(4) [2.034(4)], Ru–N4 2.158(5) [2.162(6)], and Ru–N5 1.998(4) [2.009(4)] Å. Crystals of **1b** and **4b** used are shown in the upper right corner.

been prepared. The complexes of **1a** and **1b** have been previously characterized crystallographically [2]. The structures of complexes **1** and **4** are alike (Fig. 2). The unit cell parameters of complexes **1** and **4** are similar. The principal Ru–C and Ru–N bond lengths are close as well. The counter-anion (PF_6^-) and the diethyl ether molecule are almost identically positioned in complexes **1a/4a** or **1b/4b** relative to the $[\text{Ru}(o\text{-C}_6\text{H}_4\text{-2-py})(\text{MeCN})_4]^+$ or $[\text{Ru}(o\text{-MeC}_6\text{H}_3\text{-2-py})(\text{MeCN})_4]^+$ moieties, respectively. Various aspects of geometries of **1a** and **1b** (which are as twins of **4a** and **4b**) have been discussed previously [2]. New discussion is obviously unnecessary. It should only be mentioned that the values of R , wR_2 , and GOF for yellow complexes **1a,b** and darker **4a,b** are similar practically ruling out possibilities that **4a,b** have some cavities where contaminants might be located.

2.3. Spectral and other properties

The brownish-orange crystals of **4a** and **4b** are homogeneous; they are not covered by any pseudo-film and the surface and internal colors are identical. UV–Vis spectra of **1a** and **4a** recorded in acetonitrile are shown in Fig. 3. The brownish-orange color of **4a** has been acquired in this solvent and therefore MeCN appears the

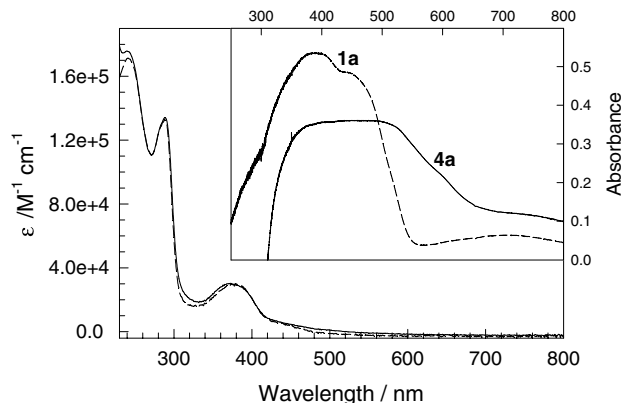


Fig. 3. UV–Vis spectra of solutions of **1a** and **4a** in MeCN. Inset shows reflectance spectra of the solid **1a** and **4a** samples. Dashed and solid lines correspond to **1a** and **4a**, respectively.

first-choice solvent. Spectral differences in solution are difficult to detect. In order to find any justification of a darker color of **4a**, it can be noticed that the extinction coefficients around 500 nm are larger for **4a**. The Beer's law holds for the both species in the concentration range $(0.425\text{--}4.25) \times 10^{-4}$ M. The spectral characteristics of solutions of **1a** and **4b** in MeCN, as well as in MeOH and CH_2Cl_2 are summarized in Table 1. Dissimilarities

Table 1
Spectral properties of complexes **1a** and **4a** obtained in different solvents

Complex	MeCN		CH_2Cl_2		MeOH	
	$\lambda(\text{max})$ (nm)	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)	$\lambda(\text{max})$ (nm)	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)	$\lambda(\text{max})$ (nm)	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)
1a	241	32 596	248	27 300	248	26 400
	288	24 924	290	24 400	290	21 200
	374	5 227	369	5 610	369	4 810
4a	241	32 093	248	38 600	248	27 900
	288	26 102	290	32 500	290	24 000
	374	5 650	369	7 959	369	5 750

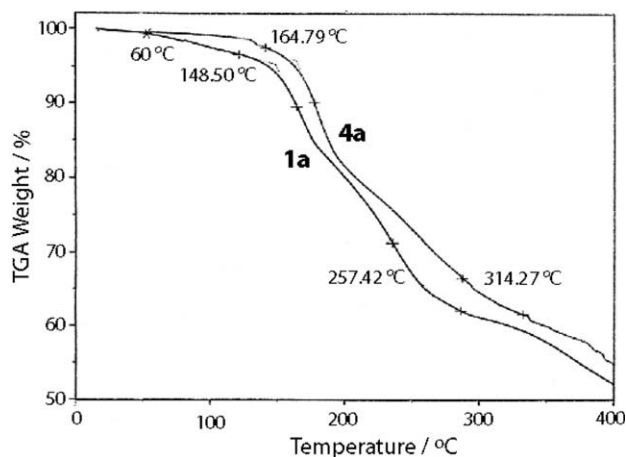


Fig. 4. TGA data for complexes **1a** and **4a** obtained at a heating rate of 10 °C/min under nitrogen.

are missing. It should be noticed that fresh-prepared solutions have been used for obtaining the UV–Vis data. Attempts have been made to minimize contacts of the solutions with air and moisture. Otherwise gradual spectral changes are observed. The solutions turn greenish and a new band around 725 nm develops. Several attempts were made to isolate this green product, but none of them was successful. Different colors of **1a** and **4a** shown in Fig. 1 are nevertheless not an optical illusion. The reflectance spectra of **1a** and **4a** are displayed as Inset to Fig. 3. The band that belongs to **4a** is significantly broader as actually should be for a strongly colored material.

Kinetic and thermodynamic reasons why complexes **1** do react with phen in MeCN but do not with bpy have been rationalized previously in terms of the dissociative ligand substitution at octahedral Ru^{II} complexes [2]. Here we confirm higher stability of complexes **4** as compared to that of **1** by the results of a thermogravimetric analysis (TGA). The data in Fig. 4 obtained for **1a** and **4a** shows that the mass loss occurs similarly for both complexes. A molecule of diethyl ether dissociates first followed by sequential loss of four MeCN ligands. The major decomposition starts at 149 and 165 °C for **1a** and **4a**, respectively. Similar temperature gap holds for **1a** and **4a** in the entire temperature range, i.e. up to 400 °C. Decomposition of **1b** (data not shown) starts at 107 °C, by 10° lower than of **4b**, but **1b** degrades a bit slower at 144–185 °C (weight loss 5–17%). Complex **4b** decomposes faster above 185 °C demonstrating the same tendency as for the **1a/4a** couple.

After all experiments performed we are still unable to rationalize chemical reasons for the unusual darkening and stabilization of complexes **1** by bpy or py when they are pseudo-converted into **4**. Speculative explanations could involve a minimization of an influence of traces of water by bpy or py molecules during the formation

of the solid phase of complexes **4**. We have been also thinking about the effect of tiny traces of iron in the ruthenium sample. Iron does not show up itself in complexes **1a,b** until the complexes are treated with bpy. 2,2'-Bipyridine does not react with **1** but ligates iron (II) to produce [Fe(bpy)₃]²⁺. This is why the material may become darker. Traces of uncomplexed iron could catalyze the oxidation of **1a,b** by dioxygen. The complex formation decreases a catalytic activity of “free” iron and therefore the stability of **4a,b** in the air is higher.

In conclusion, the complexes [Ru(*o*-C₆H₄-2-py)(MeCN)₄]PF₆ (**1a**) and [Ru(*o*-MeC₆H₃-2-py)(MeCN)₄]PF₆ (**1b**) display unusual solvent-dependent selectivity with respect to 2,2'-bipyridine and 1,10-phenanthroline. In MeCN, they react readily with phen to afford **2** but unreactive to bpy or pyridine. The yellow **1a** and **1b** complexes turn brownish-orange, become more stable but do not show major structural changes as confirmed by the X-ray crystallography.

3. Experimental

3.1. General

TGA were made using using a thermogravimetric analyzer TGA 2950. UV–Vis spectra were obtained in degassed and purified solvents using a UNICAM-UV500 spectrophotometer. Spectral data were obtained using 0.1, 0.2, and 1.0 cm cells for covering larger concentration range. Diffuse reflectance spectra for the solid samples were recorded using a Cary-5E (Varian) instrument. Other instrumentation used here is described in detail in our previous work [2].

3.2. Materials

2-Phenylpyridine and 2-(4-tolyl)pyridine were purchased from Aldrich as used a received. Other chemicals were commercially available materials usually purchased from Aldrich except RuCl₃·*n*H₂O (Strem). Starting complexes **1a,b** were made by cycloruthenation of the amines by [(η⁶-C₆H₆)RuCl(μ-Cl)]₂ as described elsewhere [2,3].

3.2.1. Synthesis of **4a** and **4b**

Complex **1a** (0.10 g, 0.18 mmol) and bpy (0.27 g, 0.18 mmol) were mixed dry in a Schlenk flask and stirred in MeCN (10 mL) at room temperature for 30 h. The color changed from yellow to brownish-orange. The resulting dark orange solution was evaporated to dryness and the residue purified by column chromatography on basic Al₂O₃ (CH₂Cl₂:MeCN = 95:5). The brownish-orange fraction was collected and evaporated in vacuum. A slow diffusion of Et₂O into a concentrated solution of the compound in CH₂Cl₂:MeCN (1:1) gave brownish-

Table 2
Crystallographic data and summary of data collection and structure refinement

	4a	4b
Formula	C ₂₃ H ₃₀ F ₆ N ₅ OPRu	C ₂₂ H ₂₇ F ₆ N ₅ O _{1/2} PRu
Formula weight	638.56	615.53
Diffractometer	Bruker Smart Apex CCD	Bruker Smart Apex CCD
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>T</i> (K)	293(2)	291(2)
<i>a</i> (Å)	8.598(1)	8.5515(7)
<i>b</i> (Å)	8.603(1)	8.7153(7)
<i>c</i> (Å)	20.172(1)	18.550(2)
α (°)	80.027(1)	97.032(2)
β (°)	78.933(1)	95.382(2)
γ (°)	81.877(1)	98.499(2)
<i>V</i> (Å ³)	1433.2(2)	1348.20(19)
<i>Z</i>	2	2
<i>D</i> _{calc} (g cm ⁻³)	1.480	1.516
θ range (°) for data collection	2.08–25.04	2.23–25.00
<i>N</i> _{measured}	16972	11 106
<i>N</i> _{independent}	5066	4753
<i>R</i>	0.0636	0.0669
<i>wR</i> ₂	0.1648	0.1450
Goodness-of-fit	1.009	0.979
Largest difference between peak and hole (e Å ⁻³)	0.980/–0.527	1.155/–0.460
Crystal size (mm ³)	0.116 × 0.144 × 0.384	0.33 × 0.16 × 0.07

orange crystals of **4a**. Yield: 75%. Stirring for 5 days at room temperature or refluxing with 2.5 equiv. of bpy gave the identical compound. The same result was obtained after stirring **1a** (0.10 g, 0.18 mmol) in 15 mL of pyridine for 15 h at room temperature. Similar purification gave the brownish-orange compound quantitatively. Complex **4b** was made similarly (75% yield). Spectral characteristics (¹H NMR, infrared, MS) of compounds **4a** and **4b** were identical to those we previously reported for **1a** and **1b** [2].

3.3. X-ray studies

Crystal data, data collection, and refinement parameters are given in Table 2. Diffraction intensity data were collected with diffractometers equipped with a graphite-monochromated Mo K α radiation source. The data collected were processed to produce conventional intensity data by the program SAINT-plus [5]. The intensity data were corrected for Lorentz and polarization effects. Absorption correction was applied using the face-indexed method. The structures were solved by direct methods and completed by subsequent difference Fourier syntheses and refined by full matrix least-squares procedures on *F*². All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated and included in the final cycle of refinement. Highly disordered PF₆ anions in some cases were modeled into two major contributors with only the common

atoms refined anisotropically. All calculations were performed by the SHELXTL (6.10) program package [6]. Crystallographic data for **4a** and **4b** have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication Nos. CCDC-269902 and CCDC-269901, respectively.

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