

# Synthesis, Properties and Molecular Structure of $[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})](\text{PF}_6)_2$ (tpm = tris(1-pyrazolyl)methane, bpy = 2,2'-bipyridine) – Another Example of Nitrile Hydrolysis Promoted by Ruthenium(II)<sup>[‡]</sup>

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The synthesis and isolation of  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})](\text{PF}_6)_2$  (tpm = tris(1-pyrazolyl)methane; bpy = 2,2'-bipyridine) in good yield is described. This new  $\text{Ru}^{\text{II}}$  complex has been spectroscopically (IR, UV/Vis, emission) and electrochemically (cyclic voltammetry) characterized. Its solid-state structure has been solved by means of X-ray diffraction analysis and shows a distorted octahedral geometry where, as expected, the tpm ligand occupies three facial coordination sites, the bpy ligand chelates two further sites, and the  $\text{CH}_3\text{CN}$  ligand saturates the coordination sphere of the Ru metal center. Electrochemical and spectroscopic results indicate that the  $\text{CH}_3\text{CN}$  ligand acts as a moderately strong  $\pi$ -acceptor. The capacity of the coordinated  $\text{CH}_3\text{CN}$  ligand to

undergo basic hydrolysis is also described. A second-order rate constant  $k_{\text{obs}} = 1.3 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$  ( $T = 25^\circ \text{C}$ ) has been obtained by following the UV/Vis absorption changes over time; the activation parameters obtained over the temperature range  $17.0\text{--}40.0^\circ \text{C}$  are:  $\Delta H^\ddagger = 74 \pm 4 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = -54 \pm 12 \text{ J mol}^{-1} \text{ K}^{-1}$ . These results are compared and discussed with regard to related complexes described in the literature that are also capable of carrying out this reaction. The results presented here make it possible to characterize the electronic and steric factors further and understand how they influence the basic hydrolysis of the coordinated  $\text{CH}_3\text{CN}$  ligand.

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## Introduction

The hydrolysis of nitriles to amides promoted by transition metals is a subject of interest with industrial and pharmacological applications.<sup>[1]</sup> Coordination of nitriles to transition metals in high or medium oxidation states normally increases the electrophilicity of the unsaturated nitrile C atom, thus promoting the addition of a great variety of

nucleophiles.<sup>[1c]</sup> When the metal ion is in a low oxidation state, promotion is usually not observed. Thus,  $\text{Ru}^{\text{III}}$  is a much better mediator than  $\text{Ru}^{\text{II}}$  for nitrile hydrolysis.<sup>[2,3]</sup> The selective hydrolysis of nitriles to amides can also be achieved electrochemically.<sup>[4]</sup>

When the coligands coordinated to  $\text{Ru}^{\text{II}}$  are strong  $\pi$ -acceptors, such as polypyridines, one would expect an enhancement of the rate constant for nitrile hydrolysis. We could demonstrate<sup>[5]</sup> a quite unusual effect for a transition metal in oxidation state +2: the  $\text{Ru}^{\text{II}}(\text{trpy})(\text{bpy})$  moiety (trpy = 2,2':6':2''-terpyridine; bpy = 2,2'-bipyridine) can accelerate the hydrolysis of acetonitrile to acetamide in basic solutions by a factor of ca.  $3 \times 10^3$ . This result was accounted for by the extensive  $\pi$ -backbonding from  $\text{Ru}^{\text{II}}$  to the polypyridyl ligands.

We describe in this work the synthesis and physicochemical properties of the  $\text{PF}_6^-$  salt of the new complex  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$  (tpm = tris(1-pyrazolyl)methane). In order to extend our knowledge of the enhancement effect of  $\text{Ru}^{\text{II}}$ , we also report on the hydrolysis of coordinated acetonitrile in this species. The structural and kinetic results obtained can be compared to those determined before for the complex  $[\text{Ru}(\text{trpy})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$ <sup>[5,6]</sup> in order to understand how the different electronic and geometric constraints influence their reactivity.

The structures of the bpy, tpm and trpy ligands are shown in Scheme 1.

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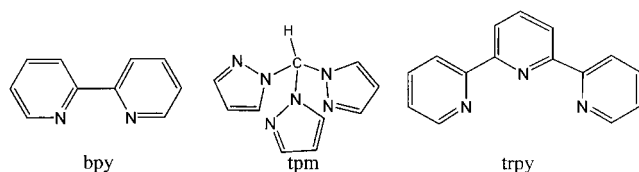
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Scheme 1.

## Results and Discussion

### Synthesis

The synthetic route to  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})](\text{PF}_6)_2$  involves the substitution of the labile  $\text{H}_2\text{O}$  ligand in the known complex  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{H}_2\text{O})](\text{PF}_6)_2$ . In order to investigate the hydrolysis in basic solutions, the  $\text{PF}_6^-$  salt was metastasized to a  $\text{Br}^-$  salt, so that a higher solubility could be achieved.

### UV/Vis and IR spectra

Figure 1 shows the electronic spectrum of  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$ . The UV spectrum in  $\text{CH}_3\text{CN}$  shows intraligand  $\pi \rightarrow \pi^*$  absorption bands between 200 and 300 nm. In the visible region, bands due to MLCT (metal-to-ligand charge transfer) transitions  $d_\pi(\text{Ru}) \rightarrow \pi^*(\text{bpy})$  are observed at  $\lambda_{\text{max}} = 397 \text{ nm}$  ( $\epsilon = 3.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 440 nm ( $\epsilon = 2.7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ). These values are lower than those corresponding to  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{py})]^{2+}$  (py = pyridine;  $\lambda_{\text{max}} = 416$  and 466 nm),<sup>[7]</sup> but similar to those of  $[\text{Ru}(\text{tpm})(\text{py})(4,4'-(\text{C}(\text{O})\text{OC}_2\text{H}_5)_2\text{-bpy})]^{2+}$  ( $\lambda_{\text{max}} = 393$  and 446 nm),<sup>[7]</sup> which leads to the conclusion that introducing a

nitrile group into the coordination sphere of the  $\text{Ru}(\text{tpm})(\text{bpy})^{2+}$  moiety has the same effect as introducing strong  $\pi$ -electron-withdrawing substituents into the 4,4'-positions of bpy. The higher  $\pi$ -acceptor capacity of  $\text{CH}_3\text{CN}$  relative to py has also been encountered when comparing the properties of  $\text{Ru}^{\text{II}}$  complexes containing 1,4,7-trithiacyclonane and 1,10-phenanthroline.<sup>[8]</sup>

On the other hand, the nitrile stretching frequency in the IR spectrum (of a KBr pellet) of  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})](\text{PF}_6)_2$  ( $\tilde{\nu}_{\text{C}\equiv\text{N}} = 2282 \text{ cm}^{-1}$ ) is shifted to a higher frequency relative to the free ligand ( $\tilde{\nu}_{\text{C}\equiv\text{N}} = 2254 \text{ cm}^{-1}$ ;  $\Delta\tilde{\nu}_{\text{C}\equiv\text{N}} = 28 \text{ cm}^{-1}$ ). If we compare this result to the decrease in  $\tilde{\nu}_{\text{C}\equiv\text{N}}$  observed in the IR spectrum of  $[\text{Ru}(\text{NH}_3)_5(\text{CH}_3\text{CN})](\text{ClO}_4)_2$ , with respect to the free ligand ( $\Delta\tilde{\nu}_{\text{C}\equiv\text{N}} = -15 \text{ cm}^{-1}$ ),<sup>[9]</sup> a strongly diminished  $\pi$ -back-bonding effect from  $\text{Ru}^{\text{II}}$  to the nitrile group caused by competition with 2,2'-bpy is inferred for the complex studied here.

### Electrochemical Measurements

The cyclic voltammetry in  $\text{CH}_3\text{CN}$ , with 0.1 M TBAH [tetrakis(*n*-butyl)ammonium hexafluorophosphate] as a supporting electrolyte shows in the oxidative range of potential a reversible redox wave for the  $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$  couple at  $E_{1/2} = 1.28 \text{ V}$  (vs. SCE). Figure S1 shows the cyclic voltammogram. The values of  $\lambda_{\text{max}}$  and  $E_{1/2}$  are consistent with those of similar complexes with strong  $\pi$ -accepting ligands, such as  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{pz})]^{2+}$  (pz = pyrazine;  $\lambda_{\text{max}} = 392$  and 457 nm;  $E_{1/2} = 1.26 \text{ V}$ ).<sup>[10]</sup>

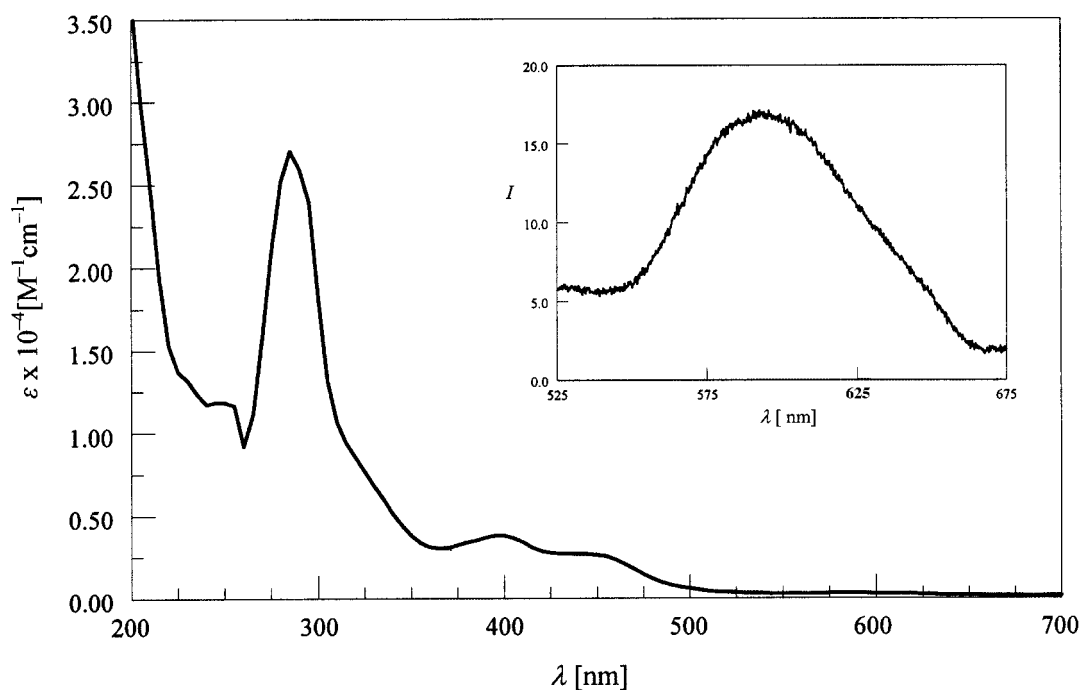


Figure 1. UV/Visible spectrum of  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$ , in  $\text{CH}_3\text{CN}$ , at room temperature. The inset shows the emission spectrum of  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$  in  $\text{CH}_3\text{CN}$ , at room temperature ( $\lambda_{\text{exc}} = 440 \text{ nm}$ ).

### Luminescence Properties

The inset in Figure 1 shows the emission spectrum of  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$  at room temperature in  $\text{CH}_3\text{CN}$ . The value of  $\lambda_{\text{em}} = 591 \text{ nm}$  (at  $\lambda_{\text{exc}} = 440 \text{ nm}$ ) is similar to that determined for  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{BPE})]^{2+}$  [ $\text{BPE} = \text{trans}$ -1,2-bis(4-pyridyl)-ethylene]:  $\lambda_{\text{em}} = 606 \text{ nm}$  at  $\lambda_{\text{exc}} = 400 \text{ nm}$  in  $\text{CH}_3\text{CN}$ <sup>[10]</sup> providing additional evidence of the behavior of  $\text{CH}_3\text{CN}$  as a stronger  $\pi$ -electron-accepting group than  $\text{py}$ .<sup>[8]</sup>

### X-ray Structure

Figure 2 shows the ORTEP diagram for the cation  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$ . The crystal data are presented in the Supporting Information. The metal center adopts a pseudo-octahedral geometry with 3 N atoms (N1, N3, N5) from the tpm ligand coordinated in a facial manner. The 2,2'-bpy (N7, N8) acts as a chelating ligand, while the sixth position is occupied by the nitrogen atom (N9) of  $\text{CH}_3\text{CN}$ .

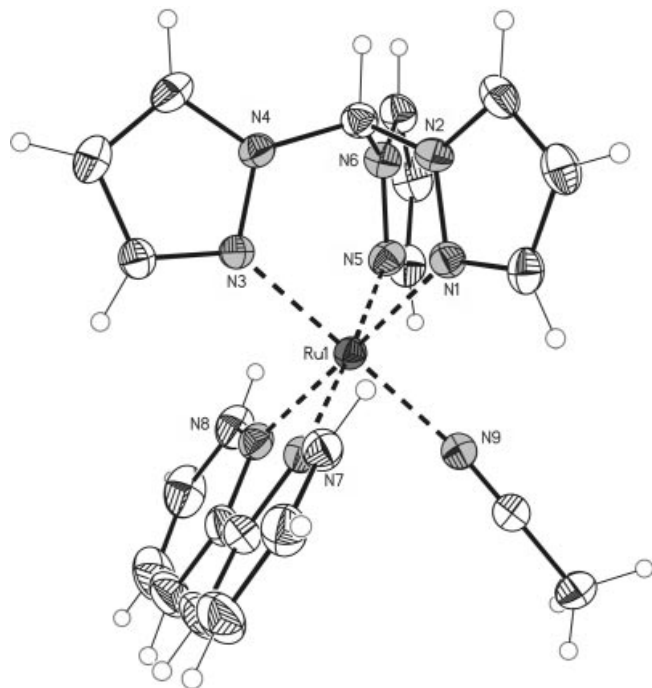


Figure 2. ORTEP-plot view (ellipsoids drawn at 50% probability) of  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$ , together with its labeling scheme. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ]:  $\text{Ru}(1)\text{--N}(9)$ , 2.0295(18);  $\text{Ru}(1)\text{--N}(7)$ , 2.044(2);  $\text{Ru}(1)\text{--N}(3)$ , 2.0500(17);  $\text{Ru}(1)\text{--N}(8)$ , 2.053(2);  $\text{Ru}(1)\text{--N}(5)$ , 2.068(2);  $\text{Ru}(1)\text{--N}(1)$ , 2.069(2);  $\text{N}(9)\text{--Ru}(1)\text{--N}(7)$ , 89.03(8);  $\text{N}(9)\text{--Ru}(1)\text{--N}(3)$ , 179.65(7);  $\text{N}(7)\text{--Ru}(1)\text{--N}(3)$ , 90.73(8);  $\text{N}(9)\text{--Ru}(1)\text{--N}(8)$ , 87.00(8);  $\text{N}(7)\text{--Ru}(1)\text{--N}(8)$ , 78.64(8);  $\text{N}(3)\text{--Ru}(1)\text{--N}(8)$ , 92.70(7);  $\text{N}(9)\text{--Ru}(1)\text{--N}(5)$ , 93.45(8);  $\text{N}(7)\text{--Ru}(1)\text{--N}(5)$ , 176.51(8);  $\text{N}(3)\text{--Ru}(1)\text{--N}(5)$ , 86.78(8);  $\text{N}(8)\text{--Ru}(1)\text{--N}(5)$ , 99.03(8);  $\text{N}(9)\text{--Ru}(1)\text{--N}(1)$ , 94.24(8);  $\text{N}(7)\text{--Ru}(1)\text{--N}(1)$ , 98.86(8);  $\text{N}(3)\text{--Ru}(1)\text{--N}(1)$ , 86.05(8);  $\text{N}(8)\text{--Ru}(1)\text{--N}(1)$ , 177.20(9);  $\text{N}(5)\text{--Ru}(1)\text{--N}(1)$ , 83.42(8).

The Ru–N bond lengths, as well as the bonding angles, are within the range found for similar complexes.<sup>[10]</sup> The  $\text{Ru}^{\text{II}}\text{--N}9$  bond length, 2.029(18)  $\text{\AA}$ , is closer to a  $\text{Ru}^{\text{III}}\text{--N}$  bond length (2.025  $\text{\AA}$  in  $[\text{Ru}(\text{NH}_3)_5(\text{PhCN})]^{3+}$ )<sup>[11]</sup> than to a

$\text{Ru}^{\text{II}}\text{--N}$  bond length (1.954  $\text{\AA}$  in  $[\text{Ru}(\text{NH}_3)_5(\text{PhCN})]^{2+}$ ).<sup>[11]</sup> The competition of bpy and  $\text{CH}_3\text{CN}$  for the electron density of  $\text{Ru}^{\text{II}}$  makes this metal more electropositive than in the corresponding ammine complexes.

### Kinetics of Nitrile Hydrolysis

Figure 3 shows the consecutive spectra obtained at  $\text{pH} = 13.0$ ,  $I = 0.1 \text{ M}$  and  $T = 25^\circ\text{C}$  of an aqueous solution of  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$ . The MLCT absorption bands at  $\lambda_{\text{max}} = 397$  and  $440 \text{ nm}$  are shifted to  $440$  and  $510 \text{ nm}$ , respectively. Isosbestic points are observed at  $410$  and  $320 \text{ nm}$ . These changes are indicative of a hydrolysis process followed by a ligand-substitution reaction. In effect, the observed rate constant is several orders of magnitude higher than that expected for a simple substitution of  $\text{CH}_3\text{CN}$ . As shown in Figure 3, the process is completed in less than 2 hours, while ligand replacements in  $\text{Ru}^{\text{II}}$  polypyridyl complexes normally take several days at room temperature.<sup>[5]</sup> The final product is coincident with that of the ion  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{OH})]^{+}$ ; in effect, when 1 drop of concentrated HCl was added to this complex, two bands developed at  $\lambda_{\text{max}} = 427$  and  $494 \text{ nm}$ , values identical to those expected for  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{OH}_2)]^{2+}$ .<sup>[12]</sup> The process is not catalytic, since the substitution rate of  $\text{H}_2\text{O}$  for  $\text{CH}_3\text{CN}$  in  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{OH}_2)]^{2+}$  is expected to be very slow.<sup>[13]</sup> It is well known<sup>[4]</sup> that coordinated amides are rapidly released from the coordination sphere of  $\text{Ru}^{\text{II}}$  and that they undergo further hydrolysis to carboxylic acids and ammonia in basic solutions.<sup>[1c,3]</sup> It should be noted, however, that the lifetime of amido-bonded complexes can be increased by using polydentate ligands such as cyclam.<sup>[14]</sup>

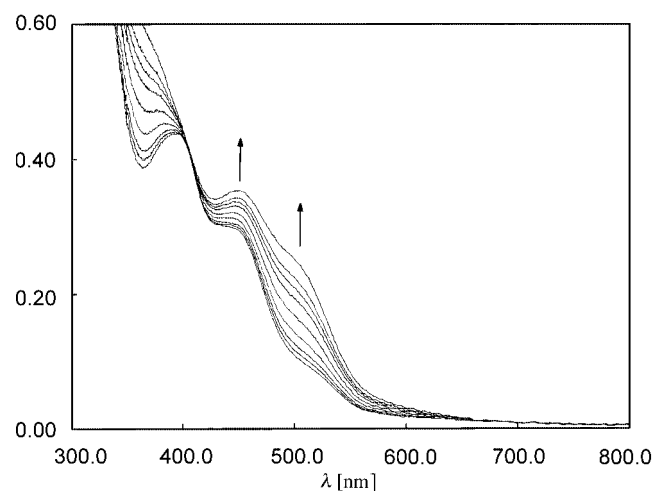


Figure 3. Spectra obtained in aqueous basic solutions of  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$  at times  $t = 0, 3, 7, 15, 27, 41, 50, 60$  and  $81 \text{ min}$  ( $[\text{Ru}] = 1.2 \times 10^{-4} \text{ M}$ ;  $\text{pH} = 13$ ;  $I = 0.1 \text{ M}$ ;  $T = 25^\circ\text{C}$ ).

The pseudo-first-order rate constants  $k_{\text{obs}}$  depend linearly on the concentration of  $\text{OH}^-$ :  $k_{\text{obs}} = k_{\text{OH}}[\text{OH}^-]$  (Figure S2). Table 1 shows the second-order rate constants for acetonitrile hydrolysis ( $k_{\text{OH}}$ ) in several Ru complexes (including that of the free ligand). As shown in Table 1, the

rate constant for the basic hydrolysis of  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})](\text{PF}_6)_2$  is  $1.3 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$  at  $25^\circ \text{C}$ . Therefore, the  $\text{Ru}^{\text{II}}(\text{tpm})(\text{bpy})$  group accelerates the reaction by a factor of  $10^3$  with respect to the free ligand, an enhancement effect that is lower than that of  $\text{Ru}^{\text{III}}(\text{NH}_3)_5$ , but higher than that of  $\text{Ru}^{\text{II}}(\text{NH}_3)_5$ . The value is also ca. 4 times lower than that of the corresponding  $\text{Ru}^{\text{II}}(\text{trpy})(\text{bpy})$  complex, although the values are within the same order of magnitude and intermediate in the wide range of hydrolysis rate constants reported in the literature.<sup>[1b]</sup>

Table 1. Rate constants for basic hydrolyses of  $\text{CH}_3\text{CN}$  in several ruthenated species, at  $25^\circ \text{C}$ .

Complex	$k_{\text{OH}}[\text{M}^{-1} \text{ s}^{-1}]$	Reference
$\text{CH}_3\text{CN}$	$1.6 \times 10^{-6}$	[2]
$[\text{Ru}(\text{NH}_3)_5(\text{CH}_3\text{CN})]^{2+}$	$< 6 \times 10^{-5}$	[2]
$[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$	$1.3 \times 10^{-3}$	This work
$[\text{Ru}(\text{trpy})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$	$4.6 \times 10^{-3}$	[4]
$[\text{Ru}(\text{NH}_3)_5(\text{CH}_3\text{CN})]^{3+}$	$2.2 \times 10^2$	[2]

The variation of  $\ln(k_{\text{OH}}/T)$  with  $1/T$  is displayed in Figure 4. From Eyring's rate equation,<sup>[15]</sup> values of  $\Delta H^\ddagger = (74 \pm 4) \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = (-54 \pm 12) \text{ J mol}^{-1} \text{ K}^{-1}$  are determined, which are typical for an associative mechanism. Metal-catalyzed nitrile hydrolyses normally have negative activation entropies, since bimolecular processes are involved.<sup>[16]</sup>

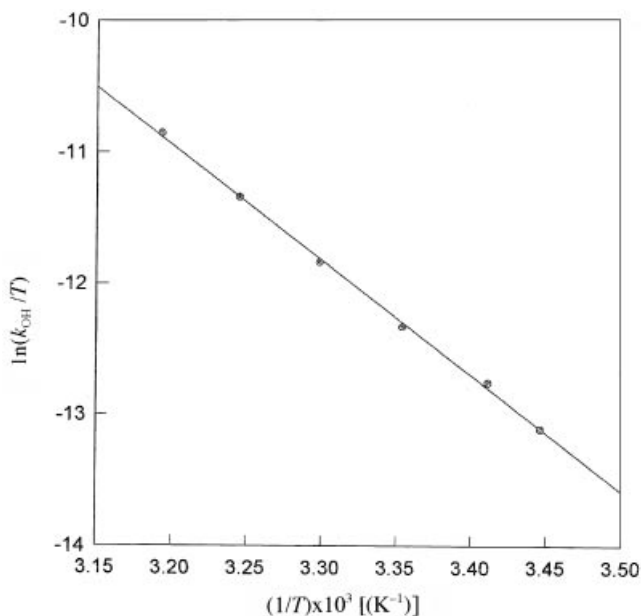


Figure 4. Eyring's plot for the basic hydrolysis of  $\text{CH}_3\text{CN}$  in  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$ .

Since trpy is a better  $\pi$ -acceptor than tpm, as evidenced by the higher  $E_{1/2}$  values of  $[\text{Ru}(\text{trpy})(\text{bpy})(\text{L})]^{2+}$  complexes than those of  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{L})]^{2+}$  complexes,<sup>[17,10]</sup> one would expect a more energy-demanding hydrolysis process for the latter species, when  $\text{L} = \text{CH}_3\text{CN}$ . However, the measured activation enthalpy is the same as that of the trpy species ( $\Delta H^\ddagger = 74 \text{ kJ mol}^{-1}$ ).<sup>[5]</sup> On the other hand, the activation entropy is highly negative and much lower than that

of the trpy species ( $\Delta S^\ddagger = -42 \text{ J mol}^{-1} \text{ K}^{-1}$ ),<sup>[5]</sup> thus accounting for its lower reaction rate. These entropy differences can be explained by considering the steric constraints imposed by the facial geometry of coordinated tpm. In contrast to the meridional geometry of trpy in  $[\text{Ru}(\text{trpy})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$ ,<sup>[6]</sup> the structure of  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$  (see Figure 2) shows that two of the tpm rings protrude out of the metal-coordinated plane containing the N1, N5, N7, and N8 atoms, thus making the attachment of the hydroxide group to the coordinated nitrile group more entropy-demanding.

## Conclusion

The new complex  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$  presents spectral, electrochemical, and photophysical properties similar to analogous species with strong  $\pi$ -electron-accepting groups. Although the  $\text{Ru}^{\text{II}}(\text{tpm})(\text{bpy})$  moiety can also promote the hydrolysis of coordinated  $\text{CH}_3\text{CN}$  by a factor of  $10^3$  relative to free  $\text{CH}_3\text{CN}$ , the effect is less than that previously observed with the  $\text{Ru}^{\text{II}}(\text{trpy})(\text{bpy})$  moiety, because of the steric constraints imposed by the facial geometry of tpm.

## Experimental Section

**Materials:** All reagents were obtained from Aldrich Chemical Co. and used without further purification.  $\text{CH}_3\text{CN}$  was freshly distilled for electrochemical measurements.

**Preparations:** All synthetic manipulations were routinely performed under nitrogen using Schlenk tubes and vacuum line techniques. Electrochemical experiments were performed in the dark under  $\text{N}_2$  or Ar with degassed solvents.

**Synthesis of  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})](\text{PF}_6)_2$ :**  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{H}_2\text{O})](\text{PF}_6)_2$  (55 mg) prepared as described before,<sup>[12]</sup> was dissolved in  $\text{CH}_3\text{CN}$  (15 mL) and refluxed for 3 h. The solution was cooled to room temperature, and diethyl ether (100 mL) was added. The orange precipitate that formed was collected on a frit, washed with cold ether, and dried in vacuo over  $\text{P}_4\text{O}_{10}$ . Yield: 36 mg (64%). Elemental analysis: calcd. C 32.9, H 2.6, N 15.7; found C 33.1, H 2.7, N 15.0. IR:  $\tilde{\nu}_{\text{C}=\text{N}} = 2282 \text{ cm}^{-1}$ . UV/Vis in  $\text{CH}_3\text{CN}$ :  $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1} \text{ cm}^{-1}$ ) = 397 ( $3.8 \times 10^3$ ), 440 ( $2.7 \times 10^3$ ), 520 ( $7.2 \times 10^2$ ).  $E_{1/2} = 1.28 \text{ V}$  (vs. SCE).

The  $\text{Br}^-$  salt of the ion  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$  was obtained by dissolving the  $\text{PF}_6^-$  salt (25 mg) in acetone (2 mL) and adding  $n\text{Bu}_4\text{NBr}$  (500 mg) previously dissolved in acetone (2 mL). The precipitate was collected by filtration, washed with cold acetone, and dried in vacuo over  $\text{P}_4\text{O}_{10}$ . Yield: 17 mg (80%).

**Equipment:** All chemicals were reagent grade and used as received. UV/Visible spectra were recorded with a Shimadzu UV-160A spectrophotometer, equipped with a thermostatted cell compartment. IR spectra (of KBr pellets) were measured using a double-beam Perkin–Elmer 983G spectrophotometer. Chemical analyses were done at INQUIMAE, University of Buenos Aires, Argentina. Fluorescence measurements were determined with a Shimadzu RF-5301 PC spectrofluorometer in  $\text{CH}_3\text{CN}$  at room temperature. Cyclic voltammetry experiments were carried out in  $\text{CH}_3\text{CN}$ , 0.1 M TBAH [tetrakis(*n*-butyl)ammonium hexafluorophosphate] on a



BAS Epsilon EC apparatus with a conventional three-electrode array, consisting of vitreous C as the working electrode, platinum wire as the auxiliary electrode and Ag/AgCl (3 M KCl) as the reference electrode. Ar was bubbled through the solutions prior to photo-physical and electrochemical measurements.

Doubly distilled water was used for all kinetic determinations. pH measurements were carried out with a precision of  $\pm 0.05$  pH units, using a Metrohm 744 pH meter. The hydrolysis reactions were studied under pseudo-first-order conditions at temperatures between 17 °C and 40 °C, and pH values between 12.1 and 13.1 (NaOH). The ionic strength was fixed at  $I = 0.1$  M (KCl). A fresh solution of  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})](\text{Br})_2$  in water was used for each set of experiments. Absorbance ( $A$ ) vs. time ( $t$ ) data were recorded at  $\lambda = 510$  nm. Duplicate or triplicate runs were made at each value of pH and temperature. The pseudo-first-order rate constants were determined by least-squares fits of  $\ln(A_t - A_\infty)$  vs.  $t$ , which were linear for more than 3 half-lives. The estimated error in the base hydrolysis rate constants ( $k_{\text{OH}}$ ) is  $\pm 5\%$ .

**X-ray Structure Determination:** Crystals of  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})](\text{PF}_6)_2$  were grown by slow diffusion of diethyl ether into a concentrated solution of  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{pz})](\text{PF}_6)_2^{[10]}$  in  $\text{CH}_3\text{CN}$  at room temperature. Molecular formula  $\text{C}_{22}\text{H}_{21}\text{F}_{12}\text{N}_9\text{P}_2\text{Ru}$ ,  $M = 802.49$ , orthorhombic,  $a = 12.88244(6)$ ,  $b = 13.4952(5)$ ,  $c = 16.3986(7)$  Å,  $V = 2850.9(2)$  Å<sup>3</sup>, space group  $P2_12_12_1$ ,  $Z = 4$ ,  $\mu = 0.775$  mm<sup>-1</sup>,  $d_{\text{calcd.}} = 1.870$  g cm<sup>-3</sup>. The measurement was made with a Siemens P4 diffractometer equipped with a SMART-CCD-1000 area detector, a MACScience Co. rotating anode with Mo- $K_\alpha$  radiation, a graphite monochromator and a Siemens low temperature device LT2 ( $T = -120$  °C). The measurements were made in the range  $1.95$  to  $31.52^\circ$ .  $44178$  reflections were collected, of which  $9061$  are unique ( $R_{\text{int}} = 0.0726$ ). Full sphere data collection  $\omega$  and  $\varphi$  scans. Programs used: Data collection Smart V. 5.060 (Bruker AXS, 1999), data reduction SAINT + Version 6.02 (Bruker AXS 1999) and absorption correction SADABS (max/min transmission:  $1.000000/0.578248$ , Bruker AXS 1999). Structure solution and refinement was performed using SHELXTL Version 5.10 (Sheldrick, Universität Göttingen, Göttingen, Germany, 1998). The structure was solved by direct methods and refined by full-matrix least-squares against  $F^2$ . All calculated hydrogen positions are free refined. Final  $R_1$  [ $I > 2\sigma(I)$ ] =  $0.0331$  and  $wR(F^2)$  [ $I > 2\sigma(I)$ ] =  $0.0719$ . The number of refined parameters was  $472$ .

CCDC-264142 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Supporting Information Available:** CIF magnetic files together with additional electrochemical (Figure S1. Cyclic voltammogram of  $[\text{Ru}(\text{tpm})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$ , in  $\text{CH}_3\text{CN}$ ,  $0.1$  M TBAH,  $\nu = 200$  mV/s) and kinetic (Figure S2. Dependence of the hydrolysis rate con-

stants  $k_{\text{obs}}$  on  $[\text{OH}^-]$ , at  $25$  °C) data (See footnote on the first page of this article.).

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