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Aust. J. Chem. **2009**, *62*, 1675–1683

Synthesis and Structure of Novel Ru^{II}–N≡C–Me Complexes and their Activity Towards Nitrile Hydrolysis: An Examination of Ligand Effects

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The synthesis and isolation of new Ru^{II}–acetonitrile complexes, of general formula *trans*,*fac*-[Ru(bpea)(B)(MeCN)]$(BF_4)_2$ (bpea = *N*,*N*-bis(2-pyridylmethyl)ethylamine; B = bpy, 2,2′-bipyridine, **4**; B = dppe, 1,2-bis(diphenylphosphino)ethane, **5**), together with a synthetic intermediate *trans*,*fac*-[Ru(NO_3)(bpea)(dppe)](BF_4), **6**, are described. Ru(bpea)Cl_3, **1**, is used as the starting material for the synthesis of all complexes **2**–**6** presented in this paper, which are characterized by analytical, spectroscopic (IR, UV/Vis, 1D and 2D NMR), and electrochemical techniques (cyclic voltammetry). Furthermore, complexes **4**, **5**, and **6** have also been characterized in the solid state by single crystal X-ray diffraction analysis. Their structures show a distorted octahedral geometry where the bpea ligand binds in a facial mode, the bidentate ligands bpy and dppe bind in a chelate manner, and finally the MeCN or the NO_3^- ligand occupy the sixth position of the octahedral Ru metal centre. The kinetics of the basic hydrolysis of the coordinated MeCN ligand for complexes **4** and **5** and for the related complex [Ru(phen)(MeCN)([9]aneS_3)]$(BF_4)_2$, **7**, which contains the 1,4,7-trithiacyclonane ligand ([9]aneS_3) and 1,10-phenanthroline (phen) is also described. Second-order rate constants for acetonitrile hydrolysis measured at 25°C of $k = 1.01 \times 10^{-3}\ M^{-1}\ s^{-1}$ for **4**, $1.08 \times 10^{-4}\ M^{-1}\ s^{-1}$ for **5**, and $6.8 \times 10^{-3}\ M^{-1}\ s^{-1}$ for **7**, have been obtained through UV-vis spectroscopy. Activation parameters have also been determined over the temperature range 25.0–45.0°C and agree with a mechanism that involves an associative rate-determining step. Finally the electronic and steric influence of the auxiliary ligands on this reaction for the above and related complexes is discussed.

Manuscript received: 23 December 2008.
Manuscript accepted: 14 May 2009.

Introduction

Ruthenium complexes are attracting a great deal of attention because of their multiple applications in many fields of science.[1] Polypyridylruthenium(II) complexes are proposed as basic electronic devices because they can act as molecular wires and switches.[2] Accordingly, they are often used as building blocks for the development of macromolecular assemblies,[3] as well as for the design and construction of molecular machines.[4] Furthermore, during the past decades, the application of ruthenium complexes as light harvesters in dye sensitized solar cells[5] has been a key issue for the development of new solar-energy conversion schemes.[6]

Catalysis is also a field in which Ru complexes have broad applications given the rich chemistry of Ru and its capacity to reach a variety of stable oxidation states depending on the ancillary ligands bonded to the first coordination sphere of the metal centre.[7] The understanding and control of these redox properties together with steric factors has led to the development of efficient catalysts for complex catalytic reactions as, for instance, water oxidation[8] or nitrile hydrolysis.[9]

The hydrolysis of nitriles to amides and carboxylic acids has significant industrial and pharmacological applications[10] and several Ru complexes have shown excellent performances in this transformation.[11] This reaction is also of biotechnological interest because nitrile hydratases, a family of non-heme iron enzymes,[12] are used in the industrial preparation of acrylamide.[13] Mechanistically, the so-called first-shell pathway that is broadly proposed at the moment is being questioned, in particular the role of Fe^{III} as a Lewis acid that activates the substrate towards nucleophilic attack.[14]

We have prepared new Ru^{II}–MeCN complexes that contain a combination of N-type and/or P-type ligands (see Fig. 1) of general formula $[Ru(bpea)(B)MeCN]^{2+}$ (bpea is the tridentate *N*,*N*-bis(2-pyridylmethyl)ethylamine; B is the bidentate bpy

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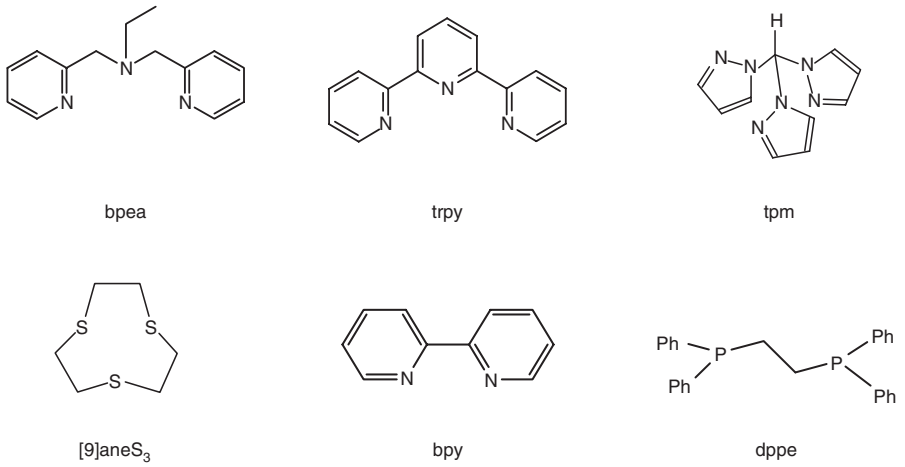
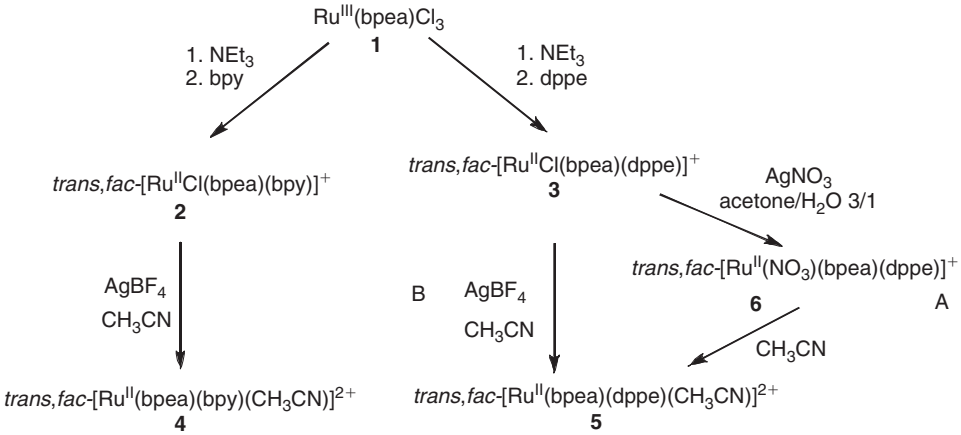


Fig. 1. Ligands used in this work.



Scheme 1.

(2,2′-bipyridine) or dppe (1,2-bis(diphenylphosphino)ethane)), with the aim of understanding how the geometric and electronic factors imposed by a combination of different ligands influence nitrile hydrolysis. These new complexes have been thoroughly characterized spectroscopically and structurally, and a kinetic analysis of the stoichiometric nitrile hydrolysis reaction in basic media has been carried out and compared with related data reported in the literature by us and others.[15]

Results and Discussion

Synthesis

The synthetic strategy followed for the preparation of Ru^{II}–NCMe complexes **4** and **5** that contain the N-tridentate facial ligand bpea and bpy or dppe, respectively, is outlined in Scheme 1. In the nomenclature used, *fac* refers to the coordination mode of the bpea (the flexibility of this ligand permits it to bond to a metal centre in either *facial* or *meridional* fashion),[7d] whereas the *cis* or *trans* prefix refers to the situation of the Ru–X (X = MeCN, Cl^-, or NO_3^-) bond with regard to the Ru–$N_{aliphatic}$(bpea) bond. The complex [Ru(bpea)Cl_3] is used as a molecularly well-defined starting material for the preparation of **2** and **3** through substitution of two labile chloro ligands by a bidentate ligand (bpy or dppe), followed by one electron reduction of the metal centre. Addition of one equivalent of Ag^I to complexes **2** and **3** in MeCN as solvent generates complexes **4** and **5** (Scheme 1, Route B) in good yields. Complex **5** is also obtained from the nitrate complex **6** in nearly quantitative yields, which in turn is obtained from the reaction of **3** and $AgNO_3$ in acetone/H_2O (3/1) as solvent.

Solid-State Structure

The crystal structures of complexes **4**, **5**, and **6** have been solved by X-ray diffraction analysis. Fig. 2 shows the *ORTEP* diagram for the cations of compounds **4**, **5**, and **6**. Table 1 and Table S1 show the crystallographic data and selected bond distances and angles, respectively. The structures show that the geometry around the Ru atom is a distorted octahedron: the bpea ligand is bonded in a facial mode whereas the bpy and dppe are bonded in a chelate manner. The sixth position is occupied by the MeCN or NO_3^- ligands that are in all cases *trans* to the aliphatic nitrogen of the bpea ligand. The two pyridyl N atoms of the bpea ligand and the two donor atoms of the bidentate ligand (either bpy or dppe) are almost coplanar, with torsion angles that range from 3.2° to 1.8° and all determine what we could define as the equatorial plane of the complexes. However, the tridentate chelating nature of the bpea ligand constrains the octahedral environment in such a way that the axis defined by the aliphatic N2 atom of the bpea ligand and the Ru metal centre is not perpendicular to the equatorial plane (as it would be in a regular octahedron, see

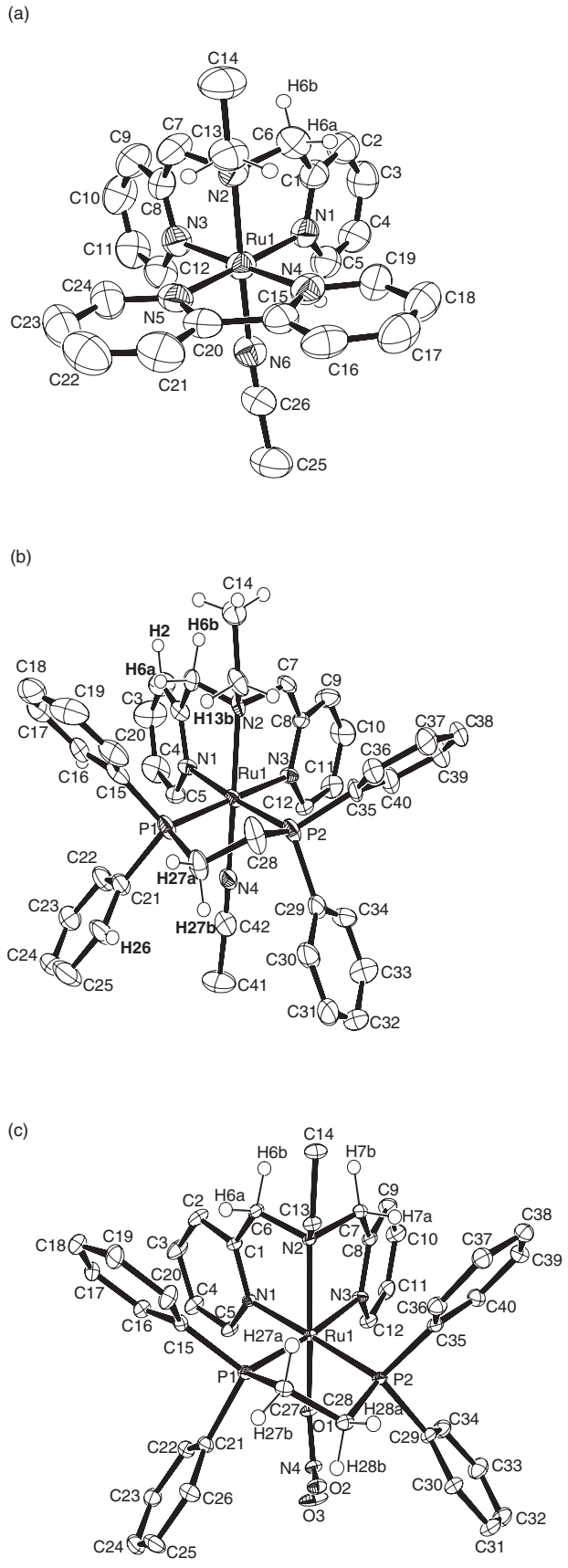


Fig. 2. X-Ray structures (ortep plots with ellipsoids at the 50% probability level) and the labelling scheme for (a) *trans*,*fac*-[Ru(bpea)(bpy)(MeCN)]$^{2+}$, **4**, (b) *trans*,*fac*-[Ru(bpea)(dppe)(MeCN)]$^{2+}$, **5**, and (c) *trans*,*fac*-[Ru(NO_3)(bpea)(dppe)]$^{+}$, **6**.

Figure S10 in the Accessory Publication). For acetonitrile complexes **4** and **5**, this effect results in a tilted axis, which keeps a rather linear arrangement between N2–Ru–$N_{acetonitrile}$. In sharp contrast, for the nitro complex **6** there is a noticeable bending of the axis probably because of hydrogen-bonding interactions between the pyridyl bpea rings and the nitro O atom bound to the metal centre (the H5–O1 and H12–O1 distances are 2.36 and 2.41 Å, respectively).

The X-ray structures of the dppe complexes **5** and **6** display an asymmetric layout for the dppe ligand and thus both independent enantiomers are found in the corresponding unit cell. This establishes a difference between the structure found in the solid state and the one in solution because NMR experiments make evident the fast interconversion between the two enantiomers, with a symmetrical attribution of the signals for the dppe ligand (see Experimental section for NMR assignments). Bond distances and angles are within the range found for related complexes.[15–25]

Spectroscopic and Redox Properties

The 1D and 2D NMR spectra of complexes **4**, **5**, and **6** were recorded in (D_6)acetone, and are assigned in the Experimental section, and shown in the Accessory Publication. All the resonances of the complexes can be unequivocally assigned and confirm that their structure in solution is the same as in the solid state, as expected for a Ru^{II} low-spin d^6 type of metal ion. In complexes **4**, **5**, and **6** the benzylic hydrogen atoms (H6a, H6b) become magnetically different when the ligand is coordinated to the metal and are assigned as a result of an intra-ligand (bpea) NOE H6a–H13 that involves the ethyl group of the bpea ligand. Protons H27a and H27b in complexes **5** and **6** also become magnetically different and are assigned thanks to an intra-ligand (dppe) NOE H27b–H26.

Fig. 3 shows the electronic spectra of complexes **4** and **5** in MeCN and Fig. S5 that of **6** in CH_2Cl_2. All these complexes present ligand-based $\pi \rightarrow \pi^*$ transitions at high energies (UV) and $d\pi(Ru) \rightarrow \pi^*$(bpea and bpy)[25b] and $d\pi(Ru) \rightarrow \pi^*$(bpea and dppe)[5a] transitions at lower energies (visible). The latter $d\pi(Ru) \rightarrow \pi^*$ transitions appear at higher energies in complexes **5** and **6** when compared with **4**, as a result of a stronger π-acceptor capacity of dppe with regard to bpy, which produces a larger stabilization of the $d\pi(Ru)$ levels.[15c]

The redox potentials for the complexes **4** and **5** are obtained from cyclic voltammetry (CV) and are shown in Table 2 together with the corresponding values for related complexes of general formula [Ru(T)(B)(MeCN)]$^{2+}$ (T is trpy, bpea, or [9]aneS$_3$; B = bpy or dppe) for comparison purposes. As it can be observed (entries d–f, Table 2) for complexes that contain bpea, tris(pyrazolyl)methane (tpm), or trpy as the tridentate ligand and bpy as the bidentate one, the redox potentials are relatively similar. When trpy is replaced by the π-acceptor ligand [9]aneS$_3$ (entry g), the $E_{1/2}$ increases sharply as expected. However, when bpy is replaced by the π-acceptor dppe ligand (entry c, Table 2), the redox potential decreases instead of increasing, a phenomenon that is not well understood.

Kinetics of Nitrile Hydrolysis

The hydrolysis of bonded nitriles was investigated for the new complexes **4** and **5** described in the present work and also for the previously reported complex [Ru(phen)(MeCN)([9]aneS$_3$)]$^{2+}$, **7**, and was monitored by UV-vis spectroscopy. Fig. 4 shows the

Table 1. Crystal data for complexes 4, 5, and 6

Parameter	4	5	6
Empirical formula	$C_{26}H_{28}B_2F_8N_6Ru$	$C_{42}H_{44}BF_4N_4P_2Ru$	$C_{41}H_{43}BCl_2F_4N_4O_3P_2Ru$
Solvents in crystal	—	Omitted with squeeze[28]	$1 \times CH_2Cl_2$
Formula weight	699.23	941.44	960.51
T [K]	300(2)	153(2)	100(2)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1$
a [Å]	8.4603(12)	11.1871(5)	9.3847(10)
b [Å]	10.0484(14)	12.5839(6)	19.827(2)
c [Å]	17.197(2))	16.9391(8)	11.5098(13)
α [°]	84.194(3)	92.647(2)	90
β [°]	89.756(3)	94.396(2)	98.870(2)
γ [°]	88.805(3)	110.425(2)	90
V [Å^3]	1454.1(3)	2221.35(18)	2116.0(2)
Formula units per cell	2	2	2
ρ_{calc} [Mg m^{-3}]	1.597	1.278	1.507
μ [mm^{-1}]	0.619	0.474	0.634
R_1/wR_2 [$I > 2\sigma(I)$]	0.0680/0.1503	0.0637/0.1229	0.0562/0.1407
R_1/wR_2 (all data)	0.1331/0.1769	0.1395/0.1411	0.0628/0.1446
Goodness-of-fit (F^2)	0.952	0.815	1.140

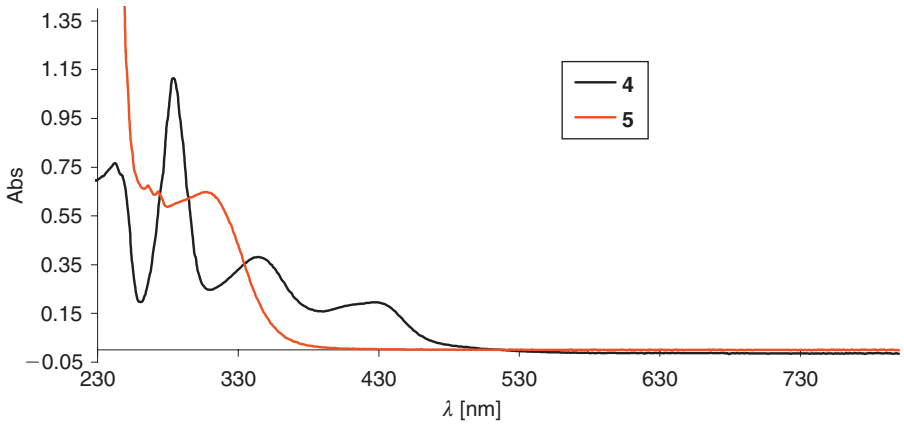


Fig. 3. UV-Vis spectra of *trans*,*fac*-[Ru(bpea)(bpy)(MeCN)]$^{2+}$, **4** and *trans*,*fac*-[Ru(bpea)(dppe)(MeCN)]$^{2+}$, **5**, recorded in MeCN, at room temperature.

consecutive spectra obtained at pH 13.0, I 0.1 M, and T 25°C of an aqueous solution of *trans*,*fac*-[Ru(bpea)(bpy)(MeCN)]$^{2+}$, **4**. The metal-to-ligand charge transfer (MLCT) absorption bands at λ_{max} 344 and 428 nm are shifted to 376 and 507 nm, respectively (in agreement with the higher π-donor character of the new anionic OH^- ligand with regard to MeCN, see below), with isosbestic points at 264, 290, 302, 354, 410, and 453 nm. The UV-vis spectra of complexes **4** and **5** in acetonitrile in the presence of 0.1 M Cl^- do not change over 3 days at room temperature, which is in agreement with the substitutionally inert nature of $Ru^{II}N_6$ (low-spin d^6) type of complexes.[19] A similar behaviour is expected for the OH^- case and thus a simple MeCN by OH^- substitution can be discarded in the present case.

The spectroscopic changes are associated with the hydrolysis of a bonded nitrile ligand followed by a ligand substitution reaction,[15c] as shown in Scheme 2.

This is further supported by the fact that amides are rapidly released from the coordination sphere of the Ru metal, and suffer further hydrolysis to carboxylic acids and ammonia.[20,21] Finally, the UV-vis spectra of the final product after hydrolysis is coincident with that of the hydroxo complex [Ru(OH)(bpea)(bpy)]$^+$ and further addition of a drop of concentrated HCl generates two bands at λ_{max} 358 and 463 nm, identical to those displayed by an authentic sample of [Ru(bpea)(bpy)(OH_2)]$^{2+}$ (Fig. S6).[25b] A similar behaviour is observed for complexes **5** and **7** (see Figs S7a and S7b) with a MLCT absorption band at λ_{max} 307 nm for **5** that shifts to 320 nm with isosbestic points at 247, 257, and 281 nm, and bands at λ_{max} 343 and 395 nm for **7** that shift to 402 and 437 nm with isosbestic points at 257, 276, and 383 nm.

The pseudo-first order rate constants k_{obs} depend linearly on [OH^-] within a concentrations range from 0.05 M to 0.2–0.3 M as shown in Fig. S9 in the Accessory Publication. Rate constants were measured in the temperature range of 25–45°C, and the corresponding plots of $\ln(k_{OH}/T)$ versus $1/T$ are displayed in Fig. S8 for complexes **4**, **5**, and **7**. From Eyring's equation,[22] values of $\Delta H^{\#}$ 76 ± 3 kJ mol^{-1} and $\Delta S^{\#}$ −47 ± 11 J mol^{-1} K^{-1} are determined for complex **4**, $\Delta H^{\#}$ 78 ± 4 kJ mol^{-1} and $\Delta S^{\#}$

Table 2. $E_{1/2}$ values and rate constants for basic hydrolysis of MeCN in several Ru^{II}–N≡C–Me complexes at 25°C

Entry	Complex	k_{OH} [M^{-1} s^{-1}]	$\Delta H^{\#}$ [kJ mol^{-1}]	$\Delta S^{\#}$ [J mol^{-1} K^{-1}]	$E_{1/2}$ [V versus SCE]	Ref.
a	MeCN	1.6×10^{-6}	—	—		[23]
b	$[Ru(NH_3)_5(MeCN)]^{2+}$	$<6 \times 10^{-5}$	—	—		[29]
c	$[Ru(bpea)(dppe)(MeCN)]^{2+}$, **5**	1.1×10^{-4}	78	−60	1.09	This work
d	$[Ru(bpea)(bpy)(MeCN)]^{2+}$, **4**	1.0×10^{-3}	76	−47	1.26	This work
e	$[Ru(tpm)(bpy)(MeCN)]^{2+}$	1.3×10^{-3}	74	−54	1.28	[15c]
f	$[Ru(trpy)(bpy)(MeCN)]^{2+}$	4.6×10^{-3}	74	−42	1.29	[20]
g	$[Ru(phen)(MeCN)([9]aneS_3)]^{2+}$, **7**	6.8×10^{-3}	69	−53	1.68	[26]

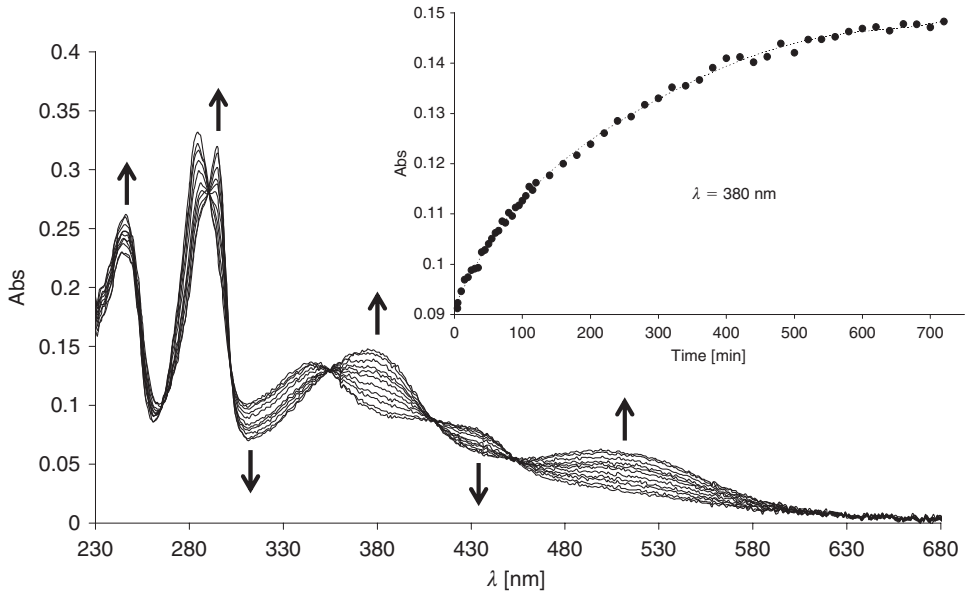
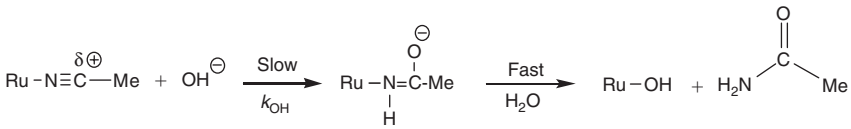


Fig. 4. Spectra obtained in aqueous basic solutions of *trans,fac*-$[Ru(bpea)(bpy)(MeCN)]^{2+}$, **4**, at times $t = 0$, 20, 50, 90, 140, 220, 320, 420, 520, and 720 min ($[Ru] = 5 \times 10^{-5}$ M, pH 13.0, I 0.1 M, T 25°C). The inset shows plots of λ 380 nm versus time during nitrile hydrolysis.



Scheme 2.

-60 ± 13 J mol^{-1} K^{-1} for complex **5**, and $\Delta H^{\#}$ 69 ± 5 kJ mol^{-1} and $\Delta S^{\#}$ -53 ± 15 J mol^{-1} K^{-1} for **7**. These values are in the range expected for an associative mechanism. Metal-catalyzed nitrile hydrolyses usually have negative activation entropies, because bimolecular processes are generally involved.[23]

A quick glance at Table 2 shows that there is a direct relationship between the Ru^{III}/Ru^{II} reduction potentials and the rate constant or the hydrolytic process; this can also be observed in Fig. 5 in a graphical manner. Thus ligands that favour the removal of electron density from the Ru^{II} metal centre in turn also reduce the electron density in the C≡N bond of the bonded MeCN ligand and, therefore, enhance the electrophilicity of the C atom where the OH^- attacks. This electronic effect is also accompanied by a significant steric effect as manifested by entries f, e, and d, where a trpy (entry f) is replaced by a tpm or bpea ligand (entries e and d, respectively), which gives rise to a very slight decrease in $E_{1/2}$ (10 mV) but a decrease of more than three-fold for the rate constant. This can be understood as a geometrical effect that involves the much larger encumbering effect of the facial tpm and bpea ligands over the Ru–N≡C–Me group with regard to that of the meridional trpy, as shown in the drawing of Fig. 6 for the trpy and bpea (**4**) cases. For complex **5**, entry c, both electronic and steric factors are unfavourable and thus generate the lowest k_{OH} value that excludes the $Ru(NH_3)_5^{2+}$ cation.

In conclusion, two new Ru^{II}–NC–Me complexes have been prepared and fully characterized and their nitrile hydolysis

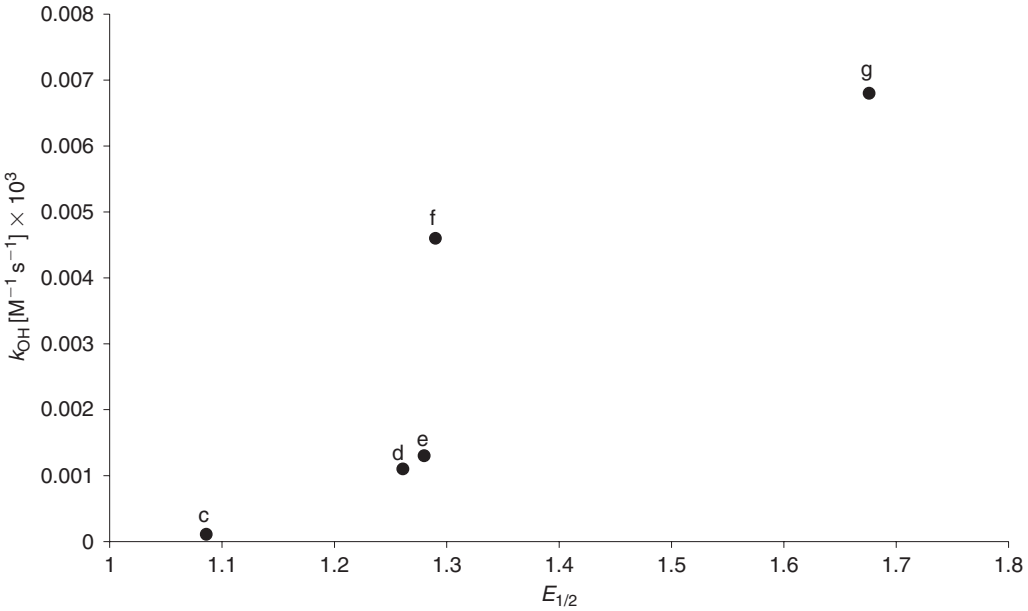


Fig. 5. Graph of $E_{1/2}$ versus k_{OH} (25°C) for the complexes prepared in the present work and related compounds previously described. Data taken from Table 2, the labels used in this graph correspond to the entries.

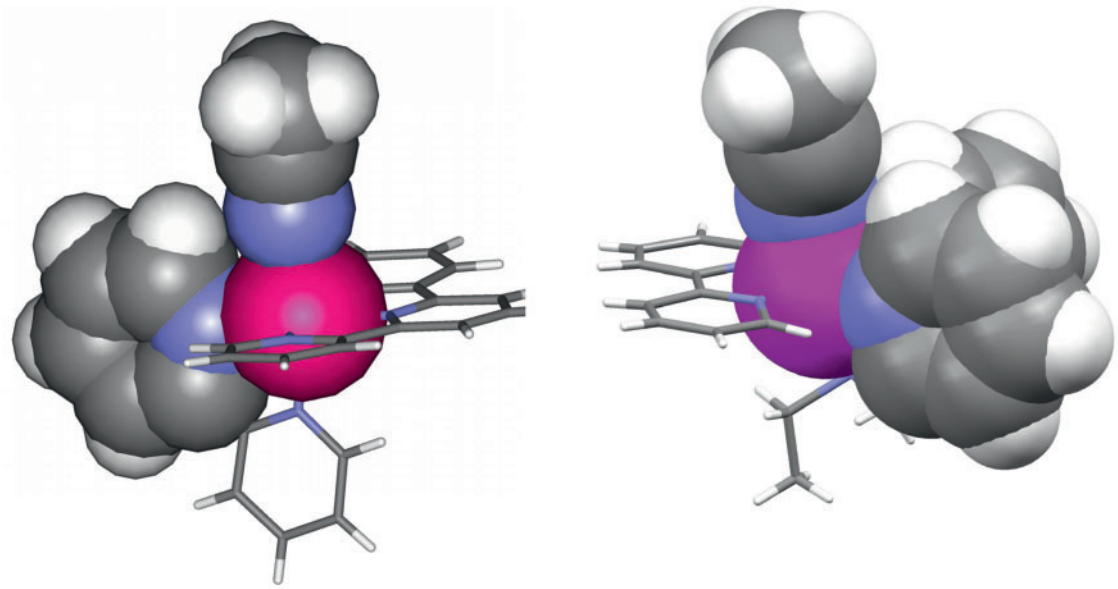


Fig. 6. Steric encumbrance comparison (schematic view) between Ru–MeCN complexes $[Ru(bpea)(bpy)(CH_3CN)]^{2+}$, **4** (right) and $[Ru(trpy)(bpy)(CH_3CN)]^{2+}$ (left).

kinetics studied together with that of **7** whose synthesis had been previously reported. The present data, together with related data previously reported in the literature, allow that rationalization of electronic and steric effects produced by the ancillary ligands over the kinetics of the nitrile hydrolysis.

Experimental

Materials

Reagent-grade organic solvents were obtained from SDS and high purity de-ionized water was obtained by passing distilled water through a nano-pure Mili-Q water purification system. $RuCl_3 \cdot 3H_2O$, **1**, was supplied by Johnson and Matthey Ltd, and was used as received. Methanol (p.a. 99%, Scharlau) was used without further purification. All other reagents used in the present work were obtained from Aldrich Chemical Co and were used without further purification.

Preparations

The bpea ligand[24] and complexes $Ru^{III}Cl_3(bpea) \cdot 2H_2O$, **1**·$2H_2O$,[25a] *trans*,*fac*-[RuCl(bpea)(bpy)](BF_4), **2**,[25b] *cis* and *trans*,*fac*-[RuCl(bpea)(dppe)](BF_4), **3**,[7a] and [Ru(phen)(MeCN)([9]aneS$_3$)]$(ClO_4)_2$[26] ([9]aneS$_3$ is 1,4,7-trithiacyclononane and phen is 1,10-phenanthroline) were prepared according to literature procedures. All synthetic manipulations were routinely performed under nitrogen atmosphere using Schlenk tubes and vacuum line techniques.

trans,fac-*[Ru(bpea)(bpy)(MeCN)](BF4)2*, ***4***

A solution that contained 68 mg (0.112 mmol) of *trans,fac*-[Ru(Cl)(bpea)(bpy)](BF_4) and 22 mg (0.112 mmol) of $AgBF_4$, in 15 mL of MeCN was refluxed for 3 h. Upon cooling to room temperature, AgCl was filtered off through a frit that contained celite and the volume of the solution removed under reduced pressure. An orange solid was obtained, which was purified by flash chromatography on an alumina column. Elution with CH_2Cl_2/MeCN, 2/1 allows one to obtain the *trans,fac*-[Ru(bpea)(bpy)(MeCN)](BF_4)$_2$, **4**. Yield: 70.5% (55 mg, 0.078 mmol). δ_H (500 MHz, (D_6)acetone, 25°C) 0.98 (t, $^3J_{14-13}$ 7, 3H, H14), 2.28 (q, $^3J_{13-14}$ 7, 2H, H13), 2.42 (s, 3H, H25), 4.44 (d, $^2J_{6a-6b}$ 16.6, 2H, H6a, H7a), 4.60 (d, $^2J_{6b-6a}$ 16.6, 2H, H6b, H7b), 7.37 (t, $^3J_{4-3} = {}^3J_{4-5}$ 6.2, 2H, H4, H11), 7.50 (d, $^3J_{2-3}$ 6.2, 2H, H2, H9), 7.56 (t, $^3J_{16-15} = {}^3J_{16-17}$ 5.6, 2H, H16, H23), 7.80 (t, $^3J_{3-2} = {}^3J_{3-4}$ 6.2, 2H, H3, H10), 8.14 (t, $^3J_{17-16} = {}^3J_{17-18}$ 5.6, 2H, H17), 8.46 (d, $^3J_{15-16}$ 5.6, 2H, H15, H24), 8.71 (d, $^3J_{18-17}$ 5.6, 2H, H18, H21), 9.11 (d, $^3J_{5-4}$ 6.2, 2H, H5, H12). δ_C (125 MHz, (D_6)acetone, 25°C) 3.1 (C26), 6.9 (C14), 58.1 (C13), 60.3 (C6), 122 (C2), 123.9 (C18), 124.7 (C4), 126.1 (C25), 127.2 (C16), 137.2 (C3), 137.5 (C17), 152 (C5), 152.7 (C15), 157.8 (C19), 161.3 (C1). NOEs: H13b with H6a, H6b with H14, H6a, and H2. ν_{max}/cm^{-1} 3087, 2987, 1465, 1049, 1031, 759. λ_{max} (MeCN, 10^{-4}M)/nm (ε, M^{-1} cm^{-1}) 283 (11084), 344 (3811), 427 (1951). $E_{1/2}$ (MeCN + 0.1 M TBAH) 1.26 V versus SSCE (Found: C 44.2, N 11.75, H 4.2. Calcd for $C_{26}H_{28}B_2F_8N_6Ru{\cdot}0.5H_2O$: C 44.09, N 11.86, H 4.12%.) For the NMR assignment we have used the same labelling scheme used in the X-ray structure shown in Fig. 1a.

trans,fac-*[Ru(NO3)(bpea)(dppe)](BF4)*, ***6***

A solution that contains 50 mg (0.059 mmol) of a mixture of *cis* and *trans,fac*-[Ru(Cl)(bpea)(dppe)](BF_4), with a molar ratio of 0.4/1, respectively, and 12 mg (0.070 mmol) of $AgNO_3$, in 25 mL of a mixture of H_2O/acetone (1/3) was refluxed for 7 h. Upon cooling to room temperature, AgCl was filtered off through a frit that contained celite. The resulting solution was stirred until the precipitation of a white product. The product was collected, washed with ether, and dried. Yield: 53% (27 mg, 0.018 mmol). δ_H (200 MHz, CD_3CN, 25°C) 0.46 (t, $^3J_{14-13}$ 7, 3H, H14), 2.32 (q, $^3J_{13-14}$ 7, 2H, H13), 2.90 (d, $^2J_{6a-6b}$ 16.2, 2H, H6a, H7a), 3.41 (m, 2H, H27a, H28a), 3.49 (m, 2H, H27b, H28b), 3.69 (d, $^2J_{6b-6a}$ 16.2, 2H, H6b, H7b), 7.30 (m, 18H, H2, H9, H16–20, H17–19, H18, H23–25, H24, H31–33, H32, H36–40, H37–39, H38), 7.62 (m, 6H, H4, H11, H22–26, H30–34), 7.91 (dt, $^3J_{3-2} = {}^3J_{3-4}$ 6.8, $^4J_{3-5}$ 1.25, 2H, H3, H10), 9.41 (d, $^3J_{5-4}$ 5.4, 2H, H5, H12). ν_{max}/cm^{-1} 3070, 2960, 2937, 2867, 1436, 1311, 1288, 1270, 1056, 1000, 756, 700. $E_{1/2}$ (CH_2Cl_2 + 0.1 M TBAH) 1.27 V versus SSCE. λ_{max} (MeCN, 10^{-4} M)/nm (ε, M^{-1} cm^{-1}) 266 (7403), 273 (7551), 293 (7889), 315 (7382). (Found: C 52.54, N 6.02, H 5.15. Calcd. for $C_{40}H_{41}BF_4N_4O_3P_2Ru{\cdot}2H_2O$: C 52.70, N 6.14, H 4.97%.) For the NMR assignment we have used the same labelling scheme used in the X-ray structure shown in Fig. 1c.

trans,fac-*[Ru(bpea)(dppe)(MeCN)](BF4)2*, ***5***

Method 1

A solution that contained 67 mg (0.079 mmol) of *trans,fac*-[Ru(Cl)(bpea)(dppe)](BF_4) and 25 mg (0.128 mmol) of $AgBF_4$, in 50 mL of MeCN was refluxed for 7 h. Upon cooling to room temperature, AgCl was filtered off through a frit that contained celite and the volume of the solution was removed under reduced pressure. A yellow solid was obtained, which was purified by flash chromatography on a silica column. Elution with CH_2Cl_2/MeCN, 2/1, allows one to obtain the *trans,fac*-[Ru(bpea)(dppe)(MeCN)](BF_4)$_2$, **5**. Yield: 74.3% (55 mg, 0.058 mmol).

Method 2

Trans,fac-[Ru(NO_3)(bpea)(dppe)](BF_4) (14 mg, 0.016 mmol) was dissolved in 30 mL of MeCN and refluxed for 4 h. Upon cooling to room temperature, 2 mL of a saturated aqueous solution of $NaBF_4$ were added, and the volume was reduced in a rotary evaporator under reduced pressure until the solution began to appear turbid. It was then cooled in an ice bath and the yellow solid obtained was filtered on a frit, washed with ether, and dried. Yield: 12.8 mg (85.4%). δ_H (500 MHz, (D_6)acetone, 25°C) 0.70 (t, $^3J_{14-13}$ 7.15, 3H, H14), 1.68 (s, 3H, H41), 2.74 (q, $^3J_{13-14}$ 7.15, 2H, H13), 3.38 (m, 2H, H27a, H28a), 3.48 (d, $^2J_{6a-6b}$ 16.62, 2H, H6a, H7a), 3.76 (m, 2H, H27b, H28b), 4.38 (d, $^2J_{6b-6a}$ 16.62, 2H, H6b, H7b), 7.42 (t, 2H, H24, H32), 7.48 (t, 2H, H18, H38), 7.52 (m, 4H, H17, H19, H37, H39), 7.55 (d, 2H, H2, H9), 7.55 (m, 4H, H23, H25, H31, H33), 7.56 (m, 4H, H22, H26, H30, H34), 7.68 (t, $^3J_{4-5} = {}^3J_{4-3}$ 6.8, 2H, H4, H11), 7.83 (dt, $^3J_{16-17} = {}^3J_{20-19}$ 7, $^3J_{16-P1} = {}^3J_{20-P1}$ 7, 4H, H16, H20, H36, H40), 8.05 (dt, $^3J_{3-2} = {}^3J_{3-4}$ 6.8, $^4J_{3-5}$ 1.25, 2H, H3, H10), 9.40 (dd, $^3J_{5-4}$ 5, $^4J_{5-3}$ 1.5, 2H, H5, H12). δ_C (125 MHz, (D_6)acetone, 190 K) 7.3 (C14), 23.6 (C27), 63.1 (C13), 68 (C6, C7), 123.2 (C2, C9), 126 (C4, C11), 130.8 (C42), 131 (C24, C32), 132 (C15–35, C17–19, C37–39, C21–29, C22–34, C23–33, C25–31, C26–30), 133 (C16–40, C20–36), 139.2 (C3, C10), 151.5 (C5, C12), 160 (C1, C8). δ_P (202 MHz, (D_6)acetone, 25°C) 56.7 (s). NOEs: H13b with H6a, H6b with H14, H6a, and H2, H27b with H26. ν_{max}/cm^{-1} 2960, 2925, 2856, 1436, 1051, 1039, 700. λ_{max} (MeCN, 10^{-4} M)/nm (ε, M^{-1} cm^{-1}) 237 (32079), 265 (8238), 273 (7859), 307 (7418). $E_{1/2}$ (MeCN + 0.1 M TBAH) 1.09 V versus SSCE. (Found: C 52.39, N 5.61, H 4.93. Calcd for $C_{42}H_{44}B_2F_8N_4P_2Ru{\cdot}H_2O$: C 52.58, N 5.83, H 4.83%.) For the NMR assignment we have used the same labelling scheme used in the X-ray structure shown in Fig. 1b.

Instrumentation and Measurements

FT-IR spectra were taken in a Mattson-Galaxy Satellite FT-IR spectrophotometer that contained a MKII Golden Gate Single Reflection ATR System. UV-Vis spectroscopy was performed on a Cary 50 Scan (Varian) UV/Vis spectrophotometer with 1 cm quartz cells or with an immersion probe of 5 mm path length. Cyclic voltammetry (CV) experiments were performed in a PAR 263A EG&G potentiostat or an IJ-Cambria ICH-660 using a three-electrode cell. Glassy carbon disk electrodes (3 mm diameter) from BAS were used as the working electrode, platinum wire as an auxiliary, and SSCE as the reference electrode. All cyclic voltammograms presented in this work were recorded under a nitrogen atmosphere and the $E_{1/2}$ values reported in this work were estimated as the average of the oxidative and reductive peak potentials ($E_{p,a} + E_{p,c}$)/2 (from the cyclic voltammogram) at a scan rate of 100 mV s^{-1} using 0.1 M TBAH (tetra(*n*-butyl)ammonium hexafluorophosphate) as supporting electrolyte in either MeCN or CH_2Cl_2 as solvent. Unless explicitly mentioned, the concentration of the complexes were ~1×10^{-3} M. NMR spectroscopy was performed on a Bruker 500 MHz or a Bruker DPX 200 MHz machine. Samples were run in CD_2Cl_2 using TMS and/or residual protons as an internal standard. Elemental analyses were performed using a CHNS-O Elemental Analyzer EA-1108 from Fisons.

Double distilled water was used for all kinetic determinations. pH measurements were carried out with a precision of ±0.05 pH units, using a Methrom 744 pHmeter. The hydrolysis reactions were studied under pseudo-first order conditions at temperatures between 25 and 45°C, and a pH value of 13 (NaOH). The ionic strength was fixed at *I* 0.1 M (KCl). A fresh solution of the complexes in water was used for each set of experiments. Absorbance (*A*) versus time (*t*) data were recorded at λ 380 nm for **4**, λ 340 nm for **5**, and λ 437 nm for **7**. Duplicate or triplicate runs were made at each pH value and temperature. The pseudo-first order rate constants were determined by least-squares fits of $\ln(A_t - A_\infty)$ versus *t* (time), which were linear for more than three half-lives. The estimated error in the base hydrolysis rate constants k_{OH} is ±5%.

X-Ray Structure Determination

Suitable crystals of **6** were grown by slow diffusion of diethyl ether into a CH_2Cl_2 solution of the compound as light-yellow plates. Suitable crystals of **4** and **5** were grown by slow diffusion of diethyl ether into a MeCN solution of the compound as orange blocks and light-yellow plates, respectively. Measurement of **4** was performed on a Bruker Smart Apex CCD diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation (λ 0.71073 Å) from an X-ray tube. Data collection: Smart V.5.631 (BrukerAXS 1997-02), data reduction: *Saint+ Version 6.36A* (Bruker AXS 2001), absorption correction: *SADABS version 2.10* (Bruker AXS 2001), and structure solution and refinement: *SHELXTL Version 6.14* (Bruker AXS 2000-2003).

Crystals of **5** and **6** were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation. Measurements were made on a Bruker–Nonius diffractometer equipped with an APPEX 2 4K CCD area detector, a FR591 rotating anode with $Mo_{K\alpha}$ radiation, Montel mirrors as monochromator, and a Kryoflex low temperature device (*T* −173°C). Full-sphere data collection was used with ω and φ scans. Data collection Apex2 V. 1.0-22 (Bruker–Nonius 2004), data reduction: *Saint+ Version 6.22* (Bruker–Nonius 2001), and absorption correction: *SADABS V. 2.10* (2003). Structure solution and refinement with *SHELXTL Version 6.10* (Sheldrick, 2000) was used.[27] For structure **5** the program *Squeeze*, implemented in *Platon*, was used in order to avoid highly disorder solvent molecules.[28] The structure of **5** contains, in addition to the omitted solvent molecules, a BF_4^- anion that is disordered in two orientations. The structure of **6** contains, in addition to the BF_4^- anion, a molecule of dichloromethane.

The crystallographic data as well as details of the structure solution and refinement procedures are reported in Table 1. CCDC 685048, 685047, 685046, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033 or by email at deposit@ccdc.cam.ac.uk.[29]

Accessory Publication

CIF files together with additional spectroscopic and electrochemical data are available from the Journal's website.

Acknowledgements

This research has been financed by MEC of Spain through projects, CTQ2006-15634, CTQ2007-60476/PPQ, CTQ2007-67918, and CSD2006-0003. J.M. is grateful for the allocation of a FI doctoral grant of the Generalitat de Catalunya. X.S. thanks MICINN for a Torres Quevedo contract. I.R. and A.L. also thank Johnson and Matthey for the loan of $RuCl_3 \cdot xH_2O$.

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