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Ru(II) complexes containing dmso and pyrazolyl ligands as catalysts for nitrile hydration in environmentally friendly media†

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The synthesis of two Ru-dmso complexes containing the ligands 2-(3-pyrazolyl)pyridine (pypz-H), and pyrazole (pz-H), [$Ru^{II}Cl_2$(pypz-H)$(dmso)_2$], (**2**) and [$Ru^{II}Cl_2$(pz-H)$(dmso)_3$], (**3**), has been described. Both complexes have been fully characterized in solution through ^{1}H-NMR and UV-Vis techniques and also in the solid state through monocrystal X-ray diffraction analysis. The redox properties of both complexes have also been studied by means of cyclic voltammetry. Exposure of **2** to visible light in acetonitrile produces a substitution of one dmso ligand by a solvent molecule generating a new complex, [$Ru^{II}Cl_2$(MeCN)-(pypz-H)(dmso)] (**4**). Also, UV-visible spectroscopy points out that complex **2** presents a thermal and photochemical substitution of dmso ligands in aqueous solution. Finally, the reactivity of complexes **2** and **3** has been tested with regard to the hydration of nitriles using water as a single solvent, displaying good efficiency and selectivity for the corresponding amide derivatives. In general, better performance is achieved with complex **3**. Reuse of these catalysts in water and glycerol has been explored for the first time in ruthenium-mediated nitrile hydration catalysis.

Introduction

Chemical transformations, as well as other industrially productive processes, are experiencing a profound transformation to meet sustainability criteria, moving from old methods to new ones developed in agreement with green chemistry principles.[1] Substitution of harmful and hazardous chemicals with others more compatible with human health and the environment is mandatory, and among these the solvent replacement is especially important since amounts of solvents are usually much larger than those of reagents and products.

Water has been much under-investigated as a solvent for chemical transformations basically because of poor solubility of organic molecules; however, water is the "ideal solvent"[2] being economical, nontoxic, noninflammable and compatible with the environment. Substitution of organic solvents by water is desirable, but it becomes especially suited for those chemical transformations in which water is one of the reagents.

On the other hand, catalyst recovery is an important topic in chemistry and, in this context, solvents are of prime importance. For homogeneous catalysts with high solubility in water, an efficient method for recycling the catalyst can be based on the higher solubility of the catalyst in the aqueous phase than in the extraction organic solvents.[3] Recently, glycerol appeared as a valuable green solvent[4,5] and has also been described as a possible solvent for the immobilization of homogeneous catalysts in a similar way.[6]

The hydration of nitriles to generate the corresponding amides is an important transformation from both academic and industrial points of view.[7] Amides not only constitute versatile building blocks in synthetic organic chemistry,[8] but also exhibit a wide range of industrial applications and pharmacological interest.[9] This reaction is also of biotechnological interest since nitrile hydratases, a family of non-heme iron enzymes,[10] are used in the industrial preparation of relevant amides, such as acrylamide, nicotinamide and 5-cyanovaleramide.[11]

Conventionally, amides have been synthesized by the hydration of nitriles, catalyzed by strong acids[12] and bases.[13] However, under these conditions, various by-products, such as carboxylic acids, are formed. Moreover, many sensitive functional groups do not endure such harsh conditions, which consequently decrease the selectivity of the reaction. Therefore, the development of efficient procedures for the synthesis

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of amides that circumvent the use of stoichiometric reagents and/or acidic and basic media is highly desirable.

Extreme acidity and basicity can be avoided by using transition-metal complexes. Activation of the CN bond occurs through coordination to the metal atom, thus enhancing the rate of the hydration step.[14] A variety of transition-metal complexes (mainly of groups 8–12) have been investigated,[15] with Murahashi's ruthenium dihydride $[RuH_2(PPh_3)_4]$,[16] Parkins's platinum hydride $[PtH(PMe_2OH)\{(PMe_2O)_2H\}]$,[17] the acetylacetonate complex *cis*-$[Ru(acac)_2(PPh_2py)_2]$[18] and the Rh(I)-based system $[\{Rh\text{-}(m\text{-}OMe)(cod)\}_2]/PCy_3$ (cod = 1,5-cyclooctadiene)[19] showing remarkable activities and selectivities under mild conditions though in all cases operating in organic media in the presence of only small amounts of water. Recently, Cadierno and others[20] developed excellent hydration protocols in pure water under neutral conditions using arene-ruthenium(II) and bis(allyl)-ruthenium(IV) containing P-donor ligands as catalysts. However, to the best of our knowledge, no report of complexes with N- or S-donor ligands applied to hydration of nitriles can be found in the literature. This prompted us to study the behaviour of two Ru–dmso compounds as catalysts in the hydration of nitriles in environmentally friendly media. These dmso compounds have been described as potent antitumor compounds[21] or as precursors for the synthesis of a large variety of compounds[22] but, although catalytic applications for Ru–dmso complexes are known,[23] they have never been used as mediator complexes in nitrile hydration.

In the present work we describe the preparation and characterization of two Ru-dmso complexes containing the nonsymmetric didentate ligand 2-(3-pyrazolyl)pyridine, pypz-H, complex **2**, or the monodentate pyrazole ligand, pz-H, complex **3** (ligands are depicted in Scheme 1). We also report the efficient hydration of different nitrile substrates to their corresponding amides in water media together with some preliminary studies for the reuse of the catalytic systems.

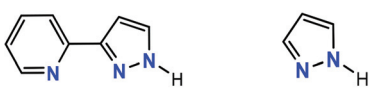
Results and discussion

Synthesis and crystal structures

The synthetic strategy followed for the preparation of the complexes described in the present paper is outlined in Scheme 1.

$[RuCl_2(dmso)_4]$ + pypz-H ⟶ *cis,cis*-$[RuCl_2(pypz\text{-}H)(dmso)_2]$
[1] **[2]**

$[RuCl_2(dmso)_4]$ + pz-H ⟶ *cis,fac*-$[RuCl_2(pz\text{-}H)(dmso)_3]$
[1] **[3]**



pypz-H **pz-H**

Scheme 1 Synthetic strategy and ligands used in this work.

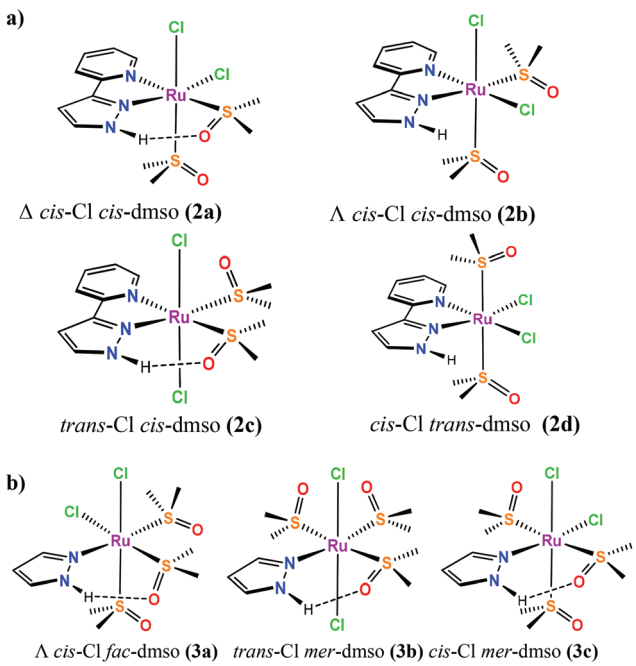
Reaction of equimolecular amounts of $[RuCl_2(dmso)_4]$, **1**, and the pypz-H or pz-H ligands in methanol or ethanol at reflux under nitrogen atmosphere produces the *cis*-Cl, *cis*-dmso complex **2** and the *cis*-Cl, *fac*-dmso complex **3**, respectively (compound **3** has been previously synthesized[24] but in this work, we introduce a new synthetic method together with a complete characterization of the complex).

In the complexes, the nomenclature *cis* or *trans* refers to the relative position of two identical monodentate ligands (Cl or dmso), and the term *fac* or *mer* is used to indicate the facial or meridional disposition of three dmso ligands.

The substitution of two dmso ligands in **1** by the unsymmetric ligand pypz-H can potentially lead to six different stereoisomers (including two pairs of enantiomers) for complex **2** which are depicted in Scheme 2a, whereas three different isomers, including one pair of enantiomers, can be formed for complex **3** (Scheme 2b).

It is remarkable that in both cases we have detected a single geometrical isomer (the pairs of enantiomers Λ/Δ-**2a** for **2** and Λ/Δ-**3a** for **3**), either when the reflux time is limited to 15′ or when it is extended up to 24 h. This fact can be rationalized taking into account the following structural and electronic factors: (a) Ru(II) is a d^6 ion; it forms strong bonds with pyridylic ligands and they do not exchange in solution with other coordinated ligands;[23c,25] (b) the existence of a strong hydrogen bonding between the oxygen atom of a dmso ligand and the pyrazolylic hydrogen atom (see below for the X-ray structure for both complexes); (c) the synergistic π-donor and π-acceptor effects between the Cl and dmso ligands mutually placed in *trans*.

The crystal structure of complex **2** has been solved by X-ray diffraction analysis. Fig. 1 displays the molecular structure of complexes **2** and **3** whereas their main crystallographic data



Scheme 2 Possible stereoisomers for **2** and **3**.

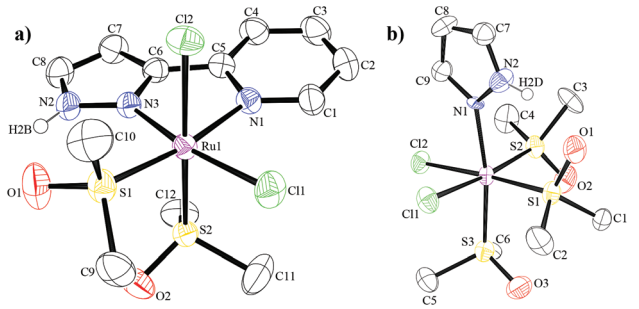


Fig. 1 Ortep plot and labeling schemes for compounds **2** and **3**.

and selected bond distances and angles can be found in the ESI section (Tables S1–S4†). In both cases, the Ru metal centers adopt an octahedrally distorted type of coordination; in complex **2** the pypz-H ligand acts in a didentate fashion and the other coordination sites are occupied by two chloro and two dmso ligands, which adopt a *cis* coordination with respect to each other. All bond distances and angles are within the expected values for this type of complexes.[21e,26]

For complex **2** it is interesting to note that the Ru–N1 bond length (2.123 Å), where the pyridyl N atom is placed *trans* to the S atom of dmso, is larger than the distance found for Ru–N3 (2.031 Å) bond, where the ligand in *trans* with respect to the pyrazole ring is a Cl atom. This denotes the stronger *trans* influence of the dmso ligand with respect to the chloro ligand, since a shorter Ru–N bond distance should be expected for the more π-acceptor pyridyl ring.

The N(1)–Ru(1)–N(3) angle is of 76.92(6)° showing the geometrical restrictions imposed by the didentate pypz-H ligand, which is considered to define the equatorial plane of the structure; as a consequence of this, the rest of the equatorial angles are larger than the 90° expected for an ideal octahedral geometry. As mentioned earlier, the complex displays strong hydrogen bonding between the oxygen atom of the equatorial dmso ligand and the hydrogen atom of the pyrazole ring (H(2b)–O(1) = 2.194 Å), then placing the methyl dmso groups above and below the equatorial plane.

The comparison of complexes **2** and **3** reveals differences in some structural parameters. For instance, it is interesting to note that the Ru–Npz bond length (Ru–N1, 2.145 Å) in **3**, where the pyrazolic ring has a dmso ligand in *trans*, is larger than the analogous distance for complex **2** (2.031 Å), again manifesting the strong *trans* influence of dmso.

Complex **3** also forms an intramolecular hydrogen bond (H(2d)–O(1) = 1.905 Å) which is stronger than the analogous bond found in complex **2**, due to the lower geometrical restrictions of the pz-H monodentate ligand with respect to the didentate pypz-H ligand.

Spectroscopic properties

The IR spectra for both complexes (see ESI†) show a band around 1092 cm^{-1} that can be assigned to a ν_{S-O} stretching, and the absence of any significant vibration in the 920–930 cm^{-1} range indicates a sulfur-bonded dmso complex,[21e,26c,e] as confirmed by the X-ray structures obtained.

The one-dimensional (1D) and two-dimensional (2D) NMR spectra of complexes **2** and **3** were recorded in CD_3CN or CD_2Cl_2 and are presented in the ESI.† The resonances found for both complexes are consistent with the structures obtained in the solid state. The complexes exhibit two sets of signals: one in the aromatic region corresponding to the nitrogen ligands and the other one in the aliphatic region assigned to the methyl groups of the bonded dmso ligands.

Complex **2** is an asymmetric molecule, and it generates four different methyl resonances due to the dmso ligands. The resonances at lower chemical shift (2 and 3.01 ppm) are assigned to the methyl groups of the axial dmso ligand, due to the anisotropic effect of the aromatic ligand over the C11 and C12 methyl groups. On the other hand, the methyl resonances of the equatorial dmso ligand are influenced by the deshielding effect of the Cl ligands over C9 and C10 methyl groups. In the aromatic part, the deshielding effect produced by the hydrogen bond between the pyrazolic hydrogen H2b and the oxygen atom of the equatorial dmso ligand allows us to identify this proton at 13.10 ppm. A similar deshielding effect is exerted by the equatorial Cl ligand over the alfa pyridyl H1 atom; the rest of the resonances are then easily identified through the COSY spectrum.

Complex **3** shows three resonances corresponding to each of the dmso ligands, with two magnetically equivalent methyl groups per ligand; a NOE effect is observed between the pyrazolic hydrogen H2d and the C3, C4 methyl groups which allows one to identify these methyl groups unambiguously; the resonances of the two remaining dmso ligands are tentatively assigned on the basis of the deshielding effect produced by the two Cl ligands.

The UV-Vis spectra for both complexes **2** and **3** are displayed in the ESI (Fig. S4†). The complexes exhibit ligand based π–π* bands below 300 nm and relatively intense bands above 300 nm mainly due to dπ–π* MLCT transitions.[27]

The redox properties of the compounds have been determined by cyclic voltammetry (CV) experiments; complex **2**, containing the didentate pypz-H ligand, exhibits a reversible monoelectronic Ru(III/II) redox wave at around 0.98 V *vs*. SSCE whereas for complex **3**, containing the monodentate pz-H ligand, the Ru(III/II) redox wave is observed at 1 V *vs*. SSCE. The higher redox potential observed for **3** arises from the stronger π-acceptor capacity of dmso with regard to the pyridyl ring present in **2** instead, though the effect is relatively scarce.

In order to obtain some information about the lability of the ligands in the synthesized complexes, we have investigated the photochemical behavior of complex **2**. A 0.65 mM solution of **2** in acetonitrile has been exposed to visible light at room temperature and its evolution has been monitored through UV-visible, NMR and cyclic voltammetric experiments. Upon exposure to light for a few minutes, the color of the solution changes from light to deep yellow, indicating the occurrence of light induced processes. In order to follow the process an 80 W lamp was used as the light source to irradiate the complex and the spectrophotometric changes were monitored using a

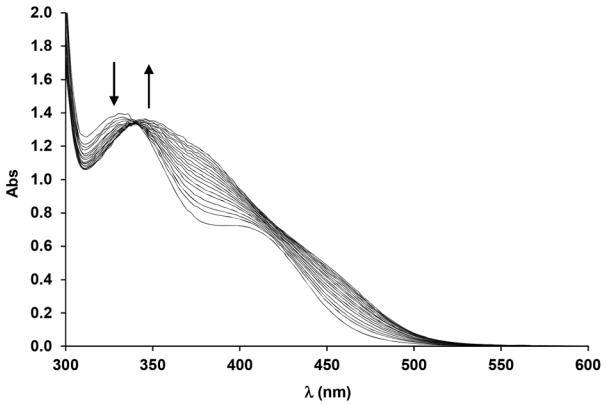


Fig. 2 UV-visible spectroscopy corresponding to the photochemical transformation of **2** into **4**.

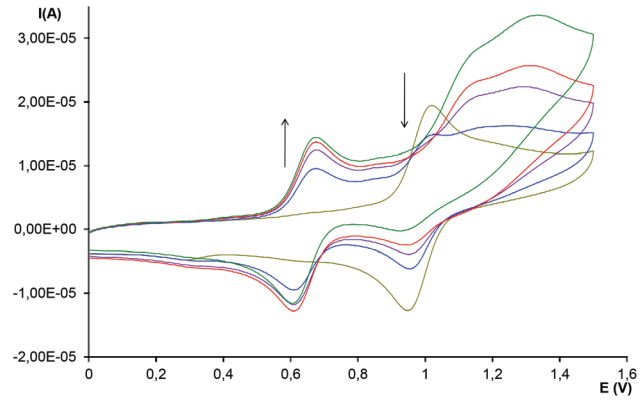


Fig. 3 Cyclic voltammograms of **2** (1 mM in a 0.1 M TBAH acetonitrile solution) after irradiation: t = 0, 21, 45, 70 and 85 minutes.

UV-Vis apparatus at 22.0 ± 0.1 °C. The evolution of the UV-Vis spectra (Fig. 2) shows one isosbestic point at 340 nm confirming the net conversion to a new compound that presumably corresponds to *cis*-[$RuCl_2$(MeCN)(pypz-H)(dmso)], **4**, as inferred from spectrophotometric, cyclic voltammetric and NMR experiments (*vide infra*). In the UV-vis spectra, a shift to lower energy absorptions is observed for the new complex **4** with regard to the initial complex **2**, as expected from the higher σ-donor and lower π-acceptor capacity of the MeCN ligand with regard to dmso, which provokes a destabilization of the dπ (Ru) donor orbital.

The changes in the ^{1}H-NMR spectrum of the aliphatic region upon **2** → **4** photochemical substitution (Fig. S5†) clearly show that free dmso (δ 2.6 ppm) is progressively generated, along with the appearance of new signals which reveal the presence of two different species during the substitution process. The four dmso singlets (located at 1.98, 2.92, 3.44 and 3.48 ppm) gradually decrease and are almost quantitatively replaced in 40 minutes by the resonances of free dmso and two new resonances at 3.38 and 3.45 ppm. From the chemical shifts of the new signals obtained, we can assert that the released dmso ligand is the one formerly occupying the axial coordination site. This is consistent with (1) the fact that the remaining equatorial dmso ligand is stabilized by H-bonding with the pyrazole ring in *cis* and (2) the axial dmso ligand is labilized thanks to a kinetic *trans* effect exerted by the Cl(2) ligand.

The substitution process has also been followed through cyclic voltammetry (CV) experiments (see Fig. 3). The initial redox wave at 0.98 V progressively decreases upon irradiation, in parallel with the appearance of a new reversible wave at 0.64 V. This value is consistent with the substitution of one dmso by MeCN since the substitution of an anionic Cl ligand by a neutral MeCN would generate much higher redox potentials.[28] The new wave observed around 1.2 V corresponds to the oxidation of free dmso.

Catalytic hydration of nitriles

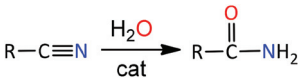
We have checked our complexes **2** and **3** in the hydration process of different nitriles under neutral conditions using water as a solvent at 80 °C. The remaining substrate has been quantified through GC chromatography with biphenyl as the internal standard and the hydrolysis products have been analysed by NMR spectroscopy and compared to pure samples of the corresponding amide and acid derivatives. Conversion and selectivity values are summarized in Table 1, together with the conditions used in the catalysis.

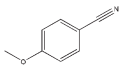
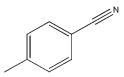
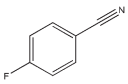
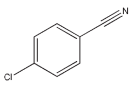
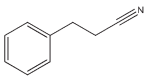
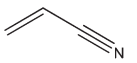
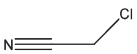
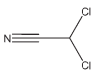
Firstly, blank experiments without any catalyst were carried out by keeping the substrates in water at 80 °C for 20 h. In all cases, the nitrile was quantitatively recovered except for the aliphatic chloronitriles (chloro and dichloroacetonitrile, entries 8 and 9), where a conversion around 40% was achieved in both cases. However, no traces of the amide product were found after the blank test for the chloroacetonitrile substrate, in contrast to the dichloroacetonitrile, where the amide was quantitatively formed. Thus, the latest substrate was not further tested in catalytic experiments.

As we can observe in Table 1, both complexes were found to be active towards nitrile hydration, with conversion values above 80% in some cases. However, the most remarkable feature is the excellent selectivity observed for the corresponding amides in the vast majority of cases, with only one exception (entry 4a) where a minor amount (lower than 10%) of the corresponding acid has been also detected. Regarding the ether substrate in entry 2, we have observed the hydrolytic cleavage of the C–O bond in the hydration reaction using **2** as a catalyst, yielding around 5% of benzonitrile. Among all the substrates tested, the hydration of acrylonitrile mediated by complex **3** is particularly interesting (entry 7), where the industrially relevant acrylamide product is quantitatively obtained.

A comparison of the conversion values displayed by the two catalysts allows concluding that, as a general trend, complex **3** (with three dmso ligands) displays higher conversion values for a larger number of substrates, though selectivity is excellent for both catalysts. The relatively higher performance of **3** could be explained by the higher flexibility of a putative intermediate species which would contain only monodentate ligands, in parallel with the occurrence of a higher number of potentially labile sites (presumably those occupied by dmso

Table 1 Ru-catalyzed hydration of nitriles to amides in water using complexes **2** and **3** as catalysts[a]



Entry	Substrate	Cat	Conv. [%]	Select.[b] [%]
1a		**2**	86[c]	>98
1b		**3**	80[c]	>98
2		**2**	36[d]	>98[d]
3a		**2**	13	>98
3b		**3**	45	>98
4a		**2**	62	90
4b		**3**	88	>98
5a		**2**	37	>98
5b		**3**	55	>98
6a		**2**	26	>98
6b		**3**	41	>98
7		**3**	61	>98
8a		**2**	85	>98
8b		**3**	53	>98
9		[e]	40	>98

[a] Reactions performed at 80 °C using 1 mmol of nitrile in 3 ml of water. [Substrate] : [Ru] ratio = 100 : 1. Time: 20 h reaction. [b] Selectivity = (amide yield/substrate conversion) × 100. [c] Amide isolated yield [%] = 75 and 71 for catalysts **2** and **3**, respectively. [d] 5% of conversion corresponds to cleavage of the ether group. Selectivity is calculated with regard to the conversion of the ether substrate. [e] Experiment was performed without a catalyst.

ligands). Decoordination of dmso is supported by the fact that free dmso is found in all cases when analysing the hydrolysis products by NMR spectroscopy.

The electronic properties of the substrates also influence the extent of the hydration reaction, provided that a nucleophilic attachment of water (or hydroxo anions) on the nitrile carbon atom takes place.[14a,b] Thus, lower performances are displayed by substrates either linked to aliphatic groups (entries 6a–b) or having *para*-electron donating groups in the aromatic ring (entries 2 and 3a–b). On the other hand, halide-substituted benzonitriles (entries 4 and 5) are expected to display better performances thanks to the electron-withdrawing character of the halide substituents (inductive effect). However, in the case of *p*-chlorobenzonitrile the performance is clearly lowered for both catalysts when compared to benzonitrile, indicating that a deactivating effect, probably caused by the resonance delocalization of the Cl lone pairs throughout the aromatic system, is taking place (the same resonance effect is expected to be much less significant for the smaller fluoride substituent). This is in contrast with the activating effect that

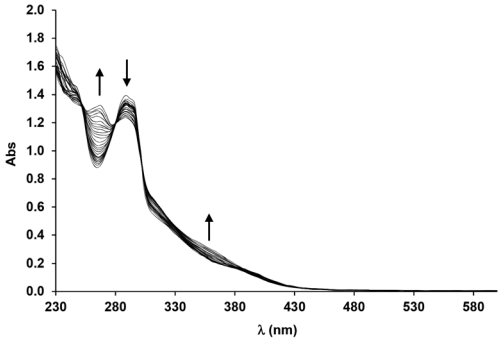


Fig. 4 Evolution of an aqueous solution of complex **2** by warming at 60 °C for 2 h. Isosbestic points are found at 280 and 302 nm.

Cl substituents have on the aliphatic substrates (entries 8 and 9), where the electronic influence is dominated by the electronegativity of the Cl substituents, leading in both cases to a considerable degree of hydrolysis without the need of a catalyst.

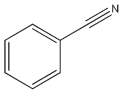
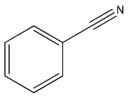
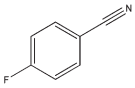
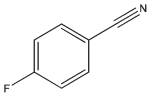
To shed some light on the changes undergone by the catalysts under the experimental conditions of the hydration process, a 0.15 mM solution of complex **2** in H_2O was kept at 60 °C and the evolution was followed by UV-vis spectroscopy. For the first 2 hours (Fig. 4), isosbestic points were found at 280 and 302 nm, thus indicating the net formation of a unique complex species presumably by substitution of a dmso ligand by water (see below). However, keeping the temperature for longer (up to 4 hours) led to the disappearance of the isosbestic points, consequently indicating that further ligand substitutions must be taking place.

A similar evolution is observed when irradiating an aqueous solution of **2** at room temperature with visible light (Fig. S7† displays the final spectra obtained after the two procedures described). However, in the case of photosubstitution the spectrum corresponding to the initial complex **2** completely vanishes within 1.5 hours, thus indicating that the photochemical substitution process is faster than the thermal one. In both cases, a new MLCT band appears at higher wavelength (around 355 nm), which is consistent with the replacement of a dmso ligand by a less π-acceptor aqua ligand.

Given the efficacy of catalysts **2** and **3** in the hydration reaction, we proceeded to test their reusabilities in water and glycerol as single solvents. As mentioned previously, glycerol appears as a valuable solvent potentially useful for the immobilization of homogeneous catalysts. In this context we have carried out a preliminary test on the reuse of these catalysts using *p*-fluorobenzonitrile and benzonitrile itself as substrates (the nitriles chosen are the ones displaying better results among the ones previously tested for each catalyst), and the results are shown in Table 2. It is notable that the amide product (which is evaluated after the last run for each set of reuses) is obtained quantitatively in all cases.

A first glance at Table 2 allows evidencing that the first run was slower in glycerol than in water for a given substrate. Both catalysts could be reused for at least a second run and, in the

Table 2 Consecutive reuses of catalysts **2** and **3** in the hydration of nitriles to amides in water and glycerol[a]

Entry	Substrate	Cat.	Solvent	Run	Conv. [%]
1		**2**	H_2O	1	86
		2	H_2O	2	35
		2	H_2O	3	49
		2	H_2O	4	20
		2	H_2O	5	2
2		**2**	Glycerol	1	62
		2	Glycerol	2	59
		2	Glycerol	3	1
3		**3**	H_2O	1	88
		3	H_2O	2	55
		3	H_2O	3	27
		3	H_2O	4	5
4		**3**	Glycerol	1	48
		3	Glycerol	2	56
		3	Glycerol	3	42
		3	Glycerol	4	2

[a] Reactions performed at 80 °C using 1 mmol of nitrile in 3 ml of water. [Substrate] : [Ru] ratio = 100 : 1. Time: 20 h reaction.

case of aqueous media, the overall turnover number was above 175 for both substrates and catalysts. However, the decrease of activity observed after the first cycle was very pronounced in water, in contrast to the case of glycerol, where both catalysts maintain their performance unaltered for a second run. Yet, the overall TON in glycerol is lower than in water (121 and 146 for entries 2 and 4 of Table 2, respectively). To the best of our knowledge, this is the first metal-based catalytic system applied to nitrile hydration catalysis in glycerol media. Although the performance obtained in glycerol is slightly lower than in water, it could also be a promising solvent for this kind of reactions.

Conclusions

In summary, we have developed two ruthenium dmso compounds for the nitrile hydration in water and glycerol media, and they have displayed very good selectivity for the amide products as well as moderate recyclability in solution. These compounds constitute the first example of ruthenium dmso compounds successfully applied to this type of reaction in environmentally friendly media, and the experiments described in glycerol are the first reported for this type of catalytic process in such a solvent.

A possible mechanism for the nitrile hydration could be initiated in the case of our catalysts by the substitution of one or more of the dmso ligands by the solvent (water in our case), as traces of free dmso are found in the NMR spectra after performing the catalytic reaction and also from the evidence found in UV-visible experiments. Thus, dmso ligands would constitute the labile coordination sites that could allow the coordination of the corresponding nitrile to the metal center. The improved efficiency of **3** *versus* **2** could arise from the easier replacement of dmso ligands in complex **3** leading to a higher number of labile coordination sites. More studies related to the mechanism are being developed in our laboratory.

Experimental procedures

Materials

All reagents used in the present work were obtained from Aldrich Chemical Co. and were used without further purification. 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. $RuCl_3{\cdot}2H_2O$ was supplied by Johnson and Matthey Ltd and was used as received.

Instrumentation and measurements

IR spectra were recorded using an ATR MK-II Golden Gate Single Reflection. UV-Vis spectroscopy was performed using a Cary 50 Scan (Varian) UV-Vis spectrophotometer with 1 cm quartz cells. Cyclic voltammetric (CV) experiments were performed using an IJ-Cambria IH-660 potentiostat using a three electrode cell. The glassy carbon electrode (3 mm diameter) from BAS was used as the working electrode, a platinum wire as the auxiliary and SSCE as the reference electrode. All cyclic voltammograms presented in this work were recorded under a nitrogen atmosphere unless explicitly mentioned. The complexes were dissolved in solvents containing the necessary amount of n-$Bu_4NH^+PF_6^-$ (TBAH) as the supporting electrolyte to yield a 0.1 M ionic strength solution. All $E_{1/2}$ values reported in this work were estimated from cyclic voltammetric experiments as the average of the oxidative and reductive peak potentials $(E_{p,a} + E_{p,c})/2$. Unless explicitly mentioned the concentration of the complexes was approximately 1 mM. ^{1}H-NMR spectroscopy was performed using a Bruker DPX 400 MHz. Samples were run in $CDCl_3$, CD_2Cl_2 or d_3-acetonitrile with internal references (residual protons and/or tetramethylsilane). Elemental analyses were performed using a CHNS-O Elemental Analyser EA-1108 from Fisons. Monochromatic irradiations were carried out using an 80 W lamp source from Phillips on complex solutions, typically 1 mM. Gas chromatography experiments were performed by capillary GC, using a GC-2010 Gas Chromatograph from Shimadzu, equipped with an Astec CHIRALDEX G-TA column (30 m × 0.25 mm diameter) incorporating a FID detector. All the product analyses in the catalytic experiments were performed by means of GC using biphenyl as the internal standard.

Crystallographic data collection and structure determination

Data collection: The measurements were carried out at 300 K using a *BRUKER SMART APEX CCD* diffractometer using graphite-monochromated Mo K_α radiation (λ = 0.71073 Å) from an X-ray tube. Full-sphere data collection was carried out with ω and φ scans. Crystals of $[Ru^{II}Cl_2(pypz\text{-}H)(dmso)_2]$ $(OH_2)_{1/2}$, (**2**), were grown from CH_2Cl_2. Crystals of $[Ru^{II}Cl_2(pz\text{-}H)(dmso)_3]$, (**3**), were grown from methanol. The measurements were made

in the range 1.96–28.30° and 2.55–28.79° for θ respectively. For compound **2** a total of 28 194 reflections were collected of which 4562 [R(int) = 0.0207] were unique. For compound **3** a total of 8492 reflections were collected of which 3561 [R(int) = 0.0229] were unique. Programs used: data collection, Smart;[29] data reduction, Saint+;[30] absorption correction, SADABS.[31] Structure solution and refinement was done using SHELXTL.[32]

The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2. The non-hydrogen atoms were refined anisotropically. The H-atoms were placed in geometrically optimized positions and forced to ride on the atom to which they are attached, except for N–H and O–H hydrogen atoms of compound **2** which were located in the difference Fourier map. The N–H hydrogen was refined freely while the O–H bond distance was constrained to 0.85(1) Å.

Preparations

The $[RuCl_2(dmso)_4]$[33] complex and the 2-(3-pyrazolyl)pyridine[34] ligand (pypz-H) were prepared according to literature procedures. All synthetic manipulations were routinely performed under a nitrogen atmosphere using Schlenk tubes and vacuum line techniques. Electrochemical experiments were performed under an N_2 atmosphere with degassed solvents. All spectroscopic, electrochemical and synthetic experiments were performed in the absence of light unless explicitly mentioned.

***cis,cis*-[$Ru^{II}Cl_2$(pypz-H)(dmso)$_2$], 2.** A 0.045 g (0.31 mmol) sample of pypz-H and 0.15 g (0.31 mmol) of $[RuCl_2(dmso)_4]$ were dissolved in 20 ml of ethanol and the resulting solution refluxed for 2 h. A light orange solid was formed and was filtered on a frit, washed with ether and vacuum-dried. Yield: 58 mg (40%). Anal. Found: C, 30.6; H, 3.98; N, 8.62; S, 13.54. Calc. for $C_{12}H_{19}Cl_2N_3O_2RuS_2$: C, 30.45; H, 4.04; N, 8.87; S, 13.54. ^{1}H-NMR (CD_2Cl_2, 400 MHz) δ 2.00 (s, 3H, H12), 3.02 (s, 3H, H11), 3.52 (s, 3H, H9), 3.54 (s, 3H, H10), 6.99 (d, 1H, H7, $J_{7,8}$ = 2.8 Hz), 7.54 (ddd, 1H, H2, $J_{2,1}$ = 6.8 Hz; $J_{2,3}$ = 7.4 Hz; $J_{2,4}$ = 1.5 Hz), 7.79 (d, 1H, H8, $J_{8,7}$ = 2.8 Hz), 7.95 (ddd, 1H, H4, $J_{4,3}$ = 7.4 Hz; $J_{4,2}$ = 1.5 Hz; $J_{4,1}$ = 0.9 Hz), 8.02(t, 1H, H3, $J_{3,2}$ = $J_{3,4}$ = 7.4 Hz; $J_{3,1}$ = 1.5 Hz), 9.43 (ddd, 1H, H1, $J_{1,2}$ = 6.8 Hz; $J_{1,3}$ = 1.5 Hz; $J_{1,4}$ = 0.9 Hz), 13.10 (s, 1H, H2B). ^{13}C-NMR ($CDCl_3$): δ 44.19, 45.12 (C11, C12), 45.59, 46.13 (C9, C10), 105.47 (C7), 122.10 (C4), 125.21 (C2), 132.06 (C8), 139.07 (C3), 151.33 (C6), 152.52 (C1, C5). For the NMR assignments we use the same labeling scheme as for the X-ray structures (Fig. 1). IR (ν_{max}, cm^{-1}): 3107, 3052, 3025, 1968, 1609, 1438, 1093, 1042, 1010, 967, 781, 681. $E_{1/2}(CH_3CN)$ = 0.98 V *vs*. SSCE. UV-Vis (CH_3CN): λ_{max}, nm (ε, M^{-1} cm^{-1}) 330 (2030), 400 (1058). ESI-MS (m/z): 438 $[M - Cl]^+$.

[$Ru^{II}Cl_2$(pz-H)(dmso)$_3$], 3. This complex was prepared through a modification of the method previously described in the literature.[24]

A 0.034 g (0.5 mmol) sample of pz-H and 0.12 g (0.25 mmol) of $[RuCl_2(dmso)_4]$ were dissolved in 10 ml of methanol and the resulting solution refluxed for 2 h. A light yellow solid was formed and was filtered on a frit, washed with methanol and vacuum-dried. Yield: 59 mg (49%). Anal. Found: C, 23.1; H, 3.9; N, 5.9. Calc. for $C_9H_{22}Cl_2N_2O_3RuS_3$: C, 23.0; H, 3.9; N, 6.0. ^{1}H-NMR (CD_2Cl_2, 400 MHz) δ 3.12 (s, 6H, H4, H3), 3.41 (s, 6H, H1, H2), 3.46 (s, 6H, H5, H6), 6.42 (dd, 1H, H8, $J_{8,9}$ = 3.02 Hz; $J_{8,7}$ = 3.78 Hz), 7.72 (dd, 1H, H7, $J_{7,8}$ = 3.78 Hz; $J_{7,9}$ = 0.9 Hz;), 8.48 (dd, 1H, H9, $J_{9,8}$ = 3.02 Hz ; $J_{9,7}$ = 0.9 Hz), 14.01 (s, 1H, H2D). ^{13}C-NMR ($CDCl_2$, 400 MHz): δ 45.97 (C5, C6), 47.20 (C1, C2), 47.71 (C3, C4), 107.40 (C8), 131.17 (C7), 142.32 (C9). For the NMR assignments we use the same labeling scheme as for the X-ray structures (Fig. 1). IR (ν_{max}, cm^{-1}): 3102, 3004, 2916, 2841, 1531, 1407, 1091, 1012, 934, 771, 674, 551. $E_{1/2}(CH_3CN)$ = 1 V *vs*. SSCE. UV-Vis (CH_3CN): λ_{max}, nm (ε, M^{-1} cm^{-1}) 354 (450).

Catalytic studies

The ruthenium catalyst (0.01 mmol), water (3 ml) and the corresponding nitrile (1 mmol) were introduced into a sealed tube and the reaction mixture was stirred at 80 °C. The nitrile was extracted with chloroform and quantified by GC, whereas the identity of the resulting amides was assessed by ^{1}H-NMR.

The catalytic reactions with glycerol were carried out under the same experimental conditions as described for water except for the extraction step which was done with CH_2Cl_2. For the recycling process, a new load of the corresponding nitrile was added to the solution after extraction with chloroform or CH_2Cl_2.

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