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# Ru(II) and Ru(IV)-dmsO complexes catalyzed efficient and selective aqueous phase nitrile hydration reactions under mild conditions

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New water soluble ruthenium(II) and (IV)-dmsO complexes [RuCl<sub>2</sub>(dmsO)<sub>2</sub>(NH<sub>3</sub>)(CH<sub>3</sub>CN)] (**1**), [RuCl<sub>2</sub>(dmsO)<sub>3</sub>(CH<sub>3</sub>CN)] (**2**), and [RuCl<sub>2</sub>(dmsO)<sub>3</sub>(NH<sub>3</sub>)]·PF<sub>6</sub>·Cl (**3**) have been synthesized and characterized by elemental analyses, IR, <sup>1</sup>H and <sup>31</sup>P NMR, and electronic absorption spectroscopy. Molecular structures of the complexes **1**, **2** and **3** were determined crystallographically. The reactivity of complexes **1-3** has been tested for aqueous phase nitrile hydration at 60°C in air, displaying good efficiency and selectivity for the corresponding amide derivatives. Best performance is achieved with complex **3**. Amide conversions of 56 to 99% were obtained with a variety of aromatic, alkyl, and vinyl nitriles. The reaction tolerated hydroxyl, nitro, bromo, formyl, pyridyl, benzyl, alkyl, and olefinic functional groups. Amides were isolated by simple decantation from the aqueous phase catalyst. Catalyst loading down to 0.0001 mol% was examined with turnover numbers as high as 990000 were observed. The catalyst was stable for weeks in solution and could be reused for more than seven times without significant loss in catalytic activity. Gram-scale reaction was also performed to produce the desired product in high yields.

## Introduction

Currently, much attention has been focused on the study of chemical transformations and other industry usable processes to meet sustainability criteria and to move away from conventional methods to new ones that meets green chemistry principles.<sup>1</sup> Now-a-days it is of utmost importance to substitute harmful and hazardous chemicals with benign chemicals others which are compatible with the environment and human health. The solvent replacement is of highest priority to be addressed, since amount of solvents used in industrial processes are usually much larger than reagents and products, and their recycling is normally 50-80% efficient.<sup>2</sup> For this reason, replacement of environmentally harmful solvents with benign non-conventional media like ionic liquids, supercritical carbon

dioxide (scCO<sub>2</sub>) and fluorinated solvents have been developed, each with its own limitations.<sup>3</sup> Water has been investigated as an ideal solvent for chemical transformations because it offers poor solubility for organic compounds, economical, non-toxic, non-inflammable and, after recovery of contaminants, it is perfectly compatible with the environment.<sup>4</sup> Consequently, it is highly desirable to develop environmentally benign processes that can be conducted in aqueous medium.<sup>5</sup> Furthermore, using water as a solvent has many advantages, such as simple operation and high efficiency in many organic reactions that involve water-soluble substrates, reagents, and renewable materials without the necessary derivatizations. The hydration reactions, where addition of water to triple bonds such as alkynes<sup>6</sup> and nitriles provides carbonyl compounds and amides, respectively. Nitrile hydration ideally represents the simplest method for the sustainable preparation of amides, employed at the industrial level for the production of acrylamide, in pharmaceutical industry<sup>7</sup> and performed also by nature in the process of nitrile assimilation by enzymes like nitrile hydratases.<sup>8</sup> The reaction between water and the nitrile moiety requires catalytic activation with either Brønsted acids or Lewis acids whose action is to bind the nitrile moiety, which becomes more electrophilic and susceptible to nucleophilic attack by water.<sup>9</sup> The reaction is usually performed under harsh experimental conditions at temperatures close or often above 100°C. So far only a few water-soluble catalysts are known for such transformations which lead to high yields under mild conditions.<sup>10</sup> A variety of transition-metal catalysts for nitrile hydration have been investigated,<sup>11</sup> however, the field is

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dominated by the use of ruthenium-based catalysts.<sup>7,9,11b,12,13-20</sup> Cadierno and others<sup>20,21</sup> developed an excellent hydration protocols in pure water under neutral conditions using arene-ruthenium(II) and bis(allyl)-ruthenium(IV) containing P-donor ligands as catalysts. In 2013, Romero *et al.* reported two Ru-dmsO complexes [RuCl<sub>2</sub>(pypz-H)(dmsO)<sub>2</sub>] and [RuCl<sub>2</sub>(pz-H)(dmsO)<sub>3</sub>] which displayed good efficiency and selectivity for the corresponding amide derivatives.<sup>21</sup> Later on Romero *et al.* developed an efficient method for the covalent anchoring of a Ru-dmsO complex onto two types of supports: mesoporous silica particles (SP) and silica coated magnetic particles (MSNP) yielding the heterogeneous systems SP@2 and MSNP@2 which were tested hydration of representative nitriles with the molecular complexes and their SP@2 and MSNP@2 as heterogeneous counterparts, in aqueous medium under neutral conditions. The heterogeneous catalysts display high yields and excellent selectivity.<sup>22</sup> In 2014, Kathó *et al.* reported a simple and efficient protocol for the synthesis of amides by the use of [RuCl<sub>2</sub>(dmsO)<sub>4</sub>] and benzylated 1,3,5-triaza-7-phosphaadamantane as catalyst.<sup>23</sup> This prompted us to study the behaviour of ruthenium(II) and (IV)-dmsO complexes [RuCl<sub>2</sub>(dmsO)<sub>2</sub>(NH<sub>3</sub>)(CH<sub>3</sub>CN)] (**1**), [RuCl<sub>2</sub>(dmsO)<sub>3</sub>(CH<sub>3</sub>CN)] (**2**), and [RuCl<sub>2</sub>(dmsO)<sub>3</sub>(NH<sub>3</sub>)]·PF<sub>6</sub>·Cl (**3**) as catalyst in the hydration of nitriles in water. The catalytic activity of ruthenium(IV)-dmsO complex is particularly effective nitrile hydration catalyst as compared to ruthenium(II)-dmsO complexes, and promising results in water have been described. As a significant improvement, herein we present first time a new Ru(IV)-dmsO complex capable of catalysing the selective hydration of a large number of organonitriles in water under remarkably milder conditions (60°C), and high activity at a low metal loading (0.0001 mol%).

## Experimental section

### Materials and Physical Measurements

All the synthetic manipulations were performed in air. The solvents were used as received without further purification. Benzonitrile, 2-methylbenzonitrile, 3-methylbenzonitrile, 4-methylbenzonitrile, 4-hydroxybenzonitrile, 4-nitrobenzonitrile, 4-bromobenzonitrile, 4-cyanobenzaldehyde, 2-cyanopyridine, 4-methylbenzyl cyanide, heptyl cyanide, pivalonitrile, acrylonitrile, ruthenium trichloride trihydrate, Ammonium hexafluorophosphate, and deuterated NMR solvents were obtained from commercial sources and used as received. The precursor complex *cis*-[RuCl<sub>2</sub>(dmsO)<sub>4</sub>]<sup>24</sup> was prepared and purified following the literature procedure. Elemental analyses were performed on a Carlo Erba Model EA-1108 elemental analyzer and data of C, H and N is within ±0.4% of calculated values. IR(KBr) was recorded using Perkin-Elmer FT-IR spectrophotometer. Electronic spectra of the **1-3** were obtained on a Perkin Elmer Lambda-35 spectrometer. <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded on a JEOL AL-400 FTNMR instrument using tetramethylsilane and phosphoric acid as an internal standard. GCMS studies were carried out with the Shimadzu-2010 instrument containing a DB-5/RtX-5MS-30Mt

& 60Mt column of 0.25mm internal diameter. M<sup>+</sup> is the mass of the cation.

### Synthesis of [RuCl<sub>2</sub>(dmsO)<sub>2</sub>(NH<sub>3</sub>)(CH<sub>3</sub>CN)] (**1**)

*Cis*-[RuCl<sub>2</sub>(dmsO)<sub>4</sub>] (0.484 g, 1 mmol) was added slowly to a solution of CH<sub>2</sub>Cl<sub>2</sub> (15 mL), and CH<sub>3</sub>CN (15 mL) containing liquid NH<sub>3</sub> (0.05 mL, 3 mmol). The resulting solution was stirred at room temperature for 12h. Slowly, the color of the solution changed from red to yellow. The resulting solution was filtered and left at room temperature for slow crystallization. In a couple of days diffraction quality crystals appeared as very fine yellow needle. These were separated and washed several times with diethyl ether, and dried. Yield: (0.270 g, 70%). Anal. Calc. for C<sub>6</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>Ru: C, 18.63; H, 4.66; N, 7.24; S, 16.57. Found: C, 18.83; H, 4.70; N, 7.41; S, 16.67. IR (cm<sup>-1</sup>, nujol):  $\nu = 3300, 3110, 2928, 2674, 2480, 1460, 1305, 1224, 1160, 1156, 1088, 1021, 980, 924, 840, 760, 704, 650, 540, 424$ . <sup>1</sup>H NMR ( $\delta$  ppm, 400 MHz, CDCl<sub>3</sub>, 298K):  $\delta$  4.00 (s, 3H), 3.36 (s, 6H), 3.30 (s, 6H), 1.99(br, 3H). UV/Vis:  $\lambda_{\max}$  ( $\epsilon$ [dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>]) = 285 (3041), 367 (8897).

### Synthesis of [RuCl<sub>2</sub>(dmsO)<sub>3</sub>(CH<sub>3</sub>CN)] (**2**)

*Cis*-[RuCl<sub>2</sub>(dmsO)<sub>4</sub>] (0.484 g, 1 mmol) was added slowly to a solution of CH<sub>3</sub>CN (30 mL). The resulting solution was stirred at room temperature for 12h. Slowly, the color of the solution changed from red to yellow. The resulting solution was filtered and left at room temperature for slow crystallization. In a couple of days diffraction quality crystals appeared as very fine yellow rod. These were separated and washed several times with diethyl ether, and dried. Yield: (0.268 g, 60%). Anal. Calc. for C<sub>8</sub>H<sub>21</sub>Cl<sub>2</sub>NO<sub>3</sub>S<sub>3</sub>Ru: C, 21.45; H, 4.69; N, 3.12; S, 21.45. Found: C, 21.61; H, 4.85; N, 3.10; S, 21.60. IR (cm<sup>-1</sup>, nujol):  $\nu = 3303, 3001, 2932, 2490, 1480, 1301, 1230, 1158, 1154, 1088, 1010, 974, 921, 840, 760, 701, 645, 521, 424$ . <sup>1</sup>H NMR ( $\delta$  ppm, 400 MHz, CDCl<sub>3</sub>, 298K):  $\delta$  3.38 (s, 6H), 3.32 (s, 6H), 3.12 (s, 6H), 1.99(br, 3H). UV/Vis:  $\lambda_{\max}$  ( $\epsilon$ [dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>]) = 299 (2760), 371(9840).

### Synthesis of [RuCl<sub>2</sub>(dmsO)<sub>3</sub>(NH<sub>3</sub>)]·PF<sub>6</sub>·Cl (**3**)

*Cis*-[RuCl<sub>2</sub>(dmsO)<sub>4</sub>] (0.484 g, 1 mmol) was added slowly to a solution of CH<sub>3</sub>OH (15 mL), and CH<sub>2</sub>Cl<sub>2</sub> (15 mL) containing liquid NH<sub>3</sub> (0.1 mL, 6 mmol). The resulting solution was stirred at room temperature for 4h. Slowly, green color precipitate appeared which was dissolved by addition of a few drop of HCl. The resulting solution was filtered through celite. Ammonium hexafluorophosphate (10 mg) dissolved in 10 mL of methanol was added to the filtrate and left at room temperature for slow crystallization. In a couple of days diffraction quality crystals appeared as very fine green needle. These were separated and washed several times with diethyl ether, and dried. Yield: (0.484 g, 80%). Anal. Calc. for C<sub>6</sub>H<sub>21</sub>Cl<sub>3</sub>F<sub>6</sub>NO<sub>3</sub>S<sub>3</sub>PRu: C, 11.87; H, 3.46; N, 2.31; S, 15.83. Found: C, 11.93; H, 3.55; N, 2.41; S, 15.91. IR (cm<sup>-1</sup>, nujol):  $\nu = 3443, 3103, 3005, 2924, 2675, 2491, 1447, 1302, 1224, 1158, 1155, 1088, 1020, 976, 923, 845, 766, 701, 651, 603, 544, 424$ . <sup>1</sup>H NMR ( $\delta$  ppm, 400 MHz, CDCl<sub>3</sub>, 298K):  $\delta$  4.00 (s, 3H), 3.35 (s, 6H), 3.31 (s, 6H), 3.10 (s, 6H). <sup>31</sup>P{<sup>1</sup>H}:  $\delta$  -144.05 (septet,

PF<sub>6</sub>); UV/Vis:  $\lambda_{\text{max}}$  ( $\epsilon$ [dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>]) = 282 (2941), 370 (8845).

### X-ray structure determination

Intensity data set for **1**, **2** and **3** were collected on oxford X-calibur S CCD area detector diffractometers using graphite monochromatized Mo-K $\alpha$  radiation at 293(2) K. The strategy for the data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard  $\phi$ -omega scan techniques, and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97, and refined by full matrix least-squares with SHELXL-97, refining on  $F^2$ .<sup>25</sup> The positions of all the atoms were obtained by direct methods. The non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were treated using appropriate riding models. The computer programme PLATON was used for analyzing the interaction and stacking distances.<sup>26</sup>

### General experimental procedure for the Catalytic Nitrile Hydration

The reaction of corresponding nitrile (1 mmol), water (3 mL), and the ruthenium catalyst [RuCl<sub>2</sub>(dms<sub>2</sub>)(NH<sub>3</sub>)(CH<sub>3</sub>CN)]/[RuCl<sub>2</sub>(dms<sub>3</sub>)(CH<sub>3</sub>CN)]/[RuCl<sub>2</sub>(dms<sub>3</sub>)(NH<sub>3</sub>)].PF<sub>6</sub>.Cl (5 mol%) were added to a Teflon-sealed screwcap culture tube and stirred at 60°C for 24h in air. After completion of the reaction as monitored by TLC, the mixture was then directly purified, without any workup, through a silica gel column by using ethyl acetate and petroleum ether as the eluent, affording the products. The identity of the resulting amides was assessed by comparison of their <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopic data with those reported in the literature and by their retention time and fragmentation from GCMS with that of an authentic sample.

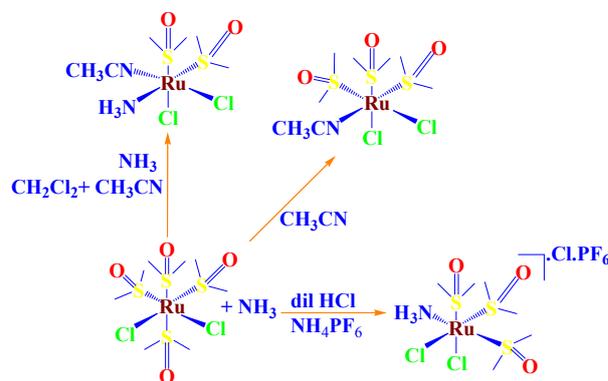
### Catalyst recycling experiments in water

The reaction of corresponding nitrile (1 mmol), water (3 mL), and the ruthenium catalyst [RuCl<sub>2</sub>(dms<sub>2</sub>)(NH<sub>3</sub>)(CH<sub>3</sub>CN)]/[RuCl<sub>2</sub>(dms<sub>3</sub>)(CH<sub>3</sub>CN)]/[RuCl<sub>2</sub>(dms<sub>3</sub>)(NH<sub>3</sub>)].PF<sub>6</sub>.Cl (5 mol%) were added to a Teflon-sealed screw-cap culture tube and stirred at 60°C for 24h in air. The conversion was obtained by taking a small aliquot (~50  $\mu$ L) from the hot solution, which after extraction with CH<sub>2</sub>Cl<sub>2</sub> (2 mL  $\times$  3) was analyzed by GCMS. After reaction completion, the solution was allowed to cool to room temperature and then placed in a refrigerator overnight, during which time the amide precipitated from solution. The aqueous supernatant containing catalyst was transferred to another reaction tube by syringe. The fresh nitrile was added to reaction tube and the tube heated to 60°C for the next hydration cycle. A small amount of cold water (~0.3 mL) and hexane (3 mL) was used to rinse the benzamide crystals and was transferred to the new tube to maximize catalyst recovery.

## Results and discussion

### Synthesis

The new complexes [RuCl<sub>2</sub>(dms<sub>2</sub>)(NH<sub>3</sub>)(CH<sub>3</sub>CN)]/[RuCl<sub>2</sub>(dms<sub>3</sub>)(CH<sub>3</sub>CN)]/[RuCl<sub>2</sub>(dms<sub>3</sub>)(NH<sub>3</sub>)].PF<sub>6</sub>.Cl (**1-3**) were synthesized in 60-80% yield from the *cis*-[RuCl<sub>2</sub>(DMSO)<sub>4</sub>] as shown in Scheme 1. The oxidation for Ru(II) complex into the Ru(IV) complex is most probably due to the presence of ubiquitous oxygen (air) in the reaction medium combined with the acidic medium employed. Complexes **1-3** were characterized by means of elemental analysis, IR and <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy, the data obtained being fully consistent with the proposed structure. Complexes **1-3** were found to be air stable, non-hygroscopic solid and soluble in water, DMF, DMSO, CH<sub>3</sub>CN and halogenated solvents. The infrared spectra of **1-3** in nujol displayed a strong band at 1088 cm<sup>-1</sup>, which has been assigned to the S-O stretching vibrations while Ru-S vibration occurred at 424 cm<sup>-1</sup>.



Scheme 1. Syntheses routes for the complexes **1-3**.

It supports linkage of dms<sub>2</sub> to the ruthenium centre through sulfur.<sup>27</sup> The band at 845 cm<sup>-1</sup> was assigned to the anion, PF<sub>6</sub><sup>-</sup> in complex **3**. In the <sup>1</sup>H NMR spectrum of complex **1**, the methyl protons of dms<sub>2</sub> resonated as two singlets for *S*-bonded dms<sub>2</sub> at 3.30-3.36 and the N-H protons of the ammine in CDCl<sub>3</sub> at  $\delta$  4.0 ppm. The methyl protons for CH<sub>3</sub>CN resonated at 1.99 ppm. However, for complexes **2** and **3**, the *S*-bonded dms<sub>3</sub> appeared as three singlets for *S*-bonded dms<sub>3</sub> at 3.10-3.38 ppm and the N-H protons of the ammine in CDCl<sub>3</sub> at  $\delta$  4.0 ppm. In <sup>31</sup>P{<sup>1</sup>H} NMR the signal due to counter ion PF<sub>6</sub><sup>-</sup> in **3** appears at -144.05 ppm in its characteristic septet pattern (see Fig. S1-S4, ESI<sup>†</sup>). The electronic spectra (Fig. 1) of complexes **1-3** in chloroform solvent showed ligand-based  $\pi$ - $\pi^*$  transitions below 300 nm and above 300 nm bands that can be assigned to MLCT transitions.<sup>28</sup>

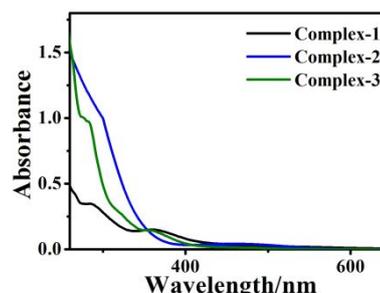
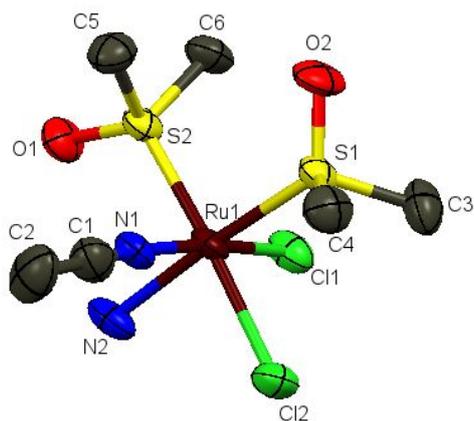


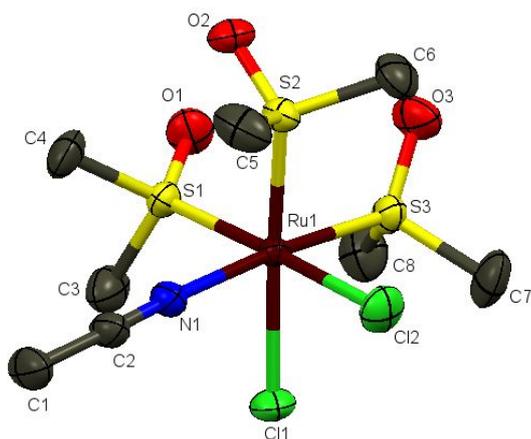
Fig. 1. UV-Vis spectra of **1-3** in CHCl<sub>3</sub>.

### Description of the Crystal Structure

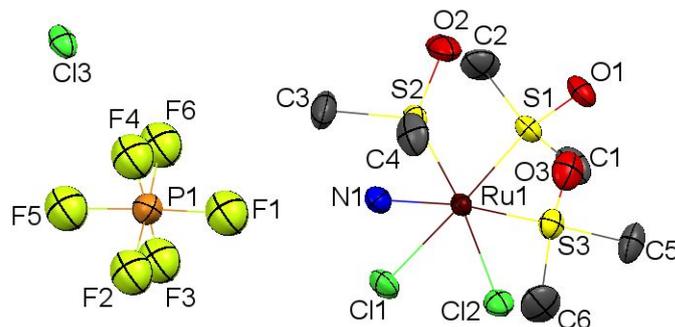
Structural data and refinement details for **1-3** are summarized in Table 1 in the ESI<sup>†</sup>. Complex **1** crystallizes in monoclinic crystal system space group,  $P2_1/n$  whereas complex **2** and **3** crystallized in orthorhombic crystal system space group,  $Pca21$  and  $Pbca$ , respectively. The coordination geometry around ruthenium centre in **1**, **2** and **3** are distorted octahedral (Fig. 3, 4 and 5). The S-bonding of all the DMSO ligands supports the suggestion that in Ru(II)-sulfoxide complexes, S-bonding is preferred to O-bonding, in the absence of trans  $\pi$ -accepting ligands and strong steric effects<sup>29</sup>.



**Fig. 2.** Molecular view of the complex **1** (thermal ellipsoids are drawn at 50% probability level). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ru(1)-N(1) 2.055(7), Ru(1)-N(2) 2.158(8), Ru(1)-S(1) 2.264(2), Ru(1)-S(2) 2.241(2), Ru(1)-Cl(1) 2.412(2), Ru(1)-Cl(2) 2.439(2), N(1)-Ru(1)-N(2) 88.3(3), N(1)-Ru(1)-S(2) 92.4(2), N(2)-Ru(1)-S(2) 88.3(2), N(1)-Ru(1)-S(1) 92.4(2), N(2)-Ru(1)-S(1) 176.3(2), S(1)-Ru(1)-S(2) 95.33(8), N(1)-Ru(1)-Cl(1) 173.87(19), N(2)-Ru(1)-Cl(1) 86.3(2), S(2)-Ru(1)-Cl(1) 90.49(8), S(1)-Ru(1)-Cl(1) 92.68(8), N(1)-Ru(1)-Cl(2) 87.5(2), N(2)-Ru(1)-Cl(2) 87.7(2), S(2)-Ru(1)-Cl(2) 175.94(8), S(1)-Ru(1)-Cl(2) 88.73(8), Cl(1)-Ru(1)-Cl(2) 89.23(9), N(1)-C(1)-C(2) 179.1(12).



**Fig. 3.** Molecular view of the complex **2** (thermal ellipsoids are drawn at 50% probability level). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ru(1)-N(1) 2.096(5), Ru(1)-S(1) 2.2786(16), Ru(1)-S(2) 2.2731(16), Ru(1)-S(3) 2.2955(16), Ru(1)-Cl(1) 2.4195(16), Ru(1)-Cl(2) 2.4381(16), N(1)-Ru(1)-S(2) 92.29(14), N(1)-Ru(1)-S(1) 89.17(13), S(1)-Ru(1)-S(2) 92.05(7), N(1)-Ru(1)-S(3) 174.29(14), S(2)-Ru(1)-S(3) 93.40(5), S(1)-Ru(1)-S(3) 91.08(5), N(1)-Ru(1)-Cl(1) 85.77(13), S(2)-Ru(1)-Cl(1) 174.09(6), S(1)-Ru(1)-Cl(1) 93.50(6), S(3)-Ru(1)-Cl(1) 88.52(6), N(1)-Ru(1)-Cl(2) 86.46(12), S(2)-Ru(1)-Cl(2) 86.99(6), S(1)-Ru(1)-Cl(2) 175.48(6), S(3)-Ru(1)-Cl(2) 93.38(6), Cl(1)-Ru(1)-Cl(2) 87.32(7), N(1)-C(1)-C(2) 177.6(7).

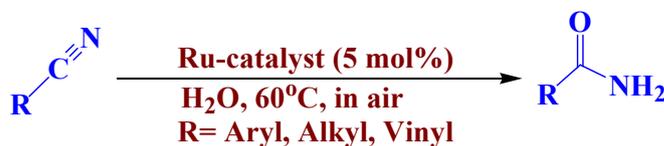


**Fig. 4.** Molecular view of the complex **3** (thermal ellipsoids are drawn at 50% probability level). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ru(1)-N(1) 2.155(5), Ru(1)-S(1) 2.2573(15), Ru(1)-S(2) 2.2655(16), Ru(1)-S(3) 2.2969(16), Ru(1)-Cl(1) 2.4309(16), Ru(1)-Cl(2) 2.4347(16), S(1)-O(1) 1.473(4), S(1)-C(2) 1.777(7), S(1)-C(1) 1.779(6), S(2)-O(2) 1.476(5), S(2)-C(4) 1.775(7), S(2)-C(3) 1.783(7), S(3)-O(3) 1.477(5), S(3)-C(6) 1.782(8), S(3)-C(5) 1.786(7), P(1)-F(1) 1.578(6), P(1)-F(4) 1.583(6), P(1)-F(6) 1.591(6), P(1)-F(2) 1.592(6), P(1)-F(3) 1.593(6), N(1)-Ru(1)-S(1) 93.47(16), N(1)-Ru(1)-S(2) 92.65(16), S(1)-Ru(1)-S(2) 91.42(6), N(1)-Ru(1)-S(3) 172.85(15), S(1)-Ru(1)-S(3) 89.46(6), S(2)-Ru(1)-S(3) 93.79(6), N(1)-Ru(1)-Cl(1) 84.22(16), S(1)-Ru(1)-Cl(1) 177.45(6), S(2)-Ru(1)-Cl(1) 87.61(6), S(3)-Ru(1)-Cl(1) 92.95(6), N(1)-Ru(1)-Cl(2) 83.46(15), S(1)-Ru(1)-Cl(2) 93.42(6), S(2)-Ru(1)-Cl(2) 173.96(6), S(3)-Ru(1)-Cl(2) 89.86(6), Cl(1)-Ru(1)-Cl(2) 87.40(6), F(1)-P(1)-F(4) 91.6(5), F(1)-P(1)-F(6) 91.7(5), F(4)-P(1)-F(6) 89.6(4), F(1)-P(1)-F(2) 90.2(5), F(4)-P(1)-F(2) 89.9(4), F(6)-P(1)-F(2) 178.1(6), F(1)-P(1)-F(3) 90.6(5), F(4)-P(1)-F(3) 177.7(5), F(6)-P(1)-F(3) 89.8(5), F(2)-P(1)-F(3) 90.6(5).

In **1**, both DMSO ligand are in equatorial position [S(1)-Ru(1)-S(2) 95.33(8)°]. The one S-atom is *trans* to Cl [S(2)-Ru(1)-Cl(2) 175.94(8)°] and the other S-atom is *trans* to NH<sub>3</sub> [N(2)-Ru(1)-S(1) 176.3(2)°]. The acetonitrile group is *trans* to other Cl [N(1)-Ru(1)-Cl(1) 173.87(19)°]. The three S-coordinated dmsol molecules adopt a *fac*-disposition in **2** and **3**, respectively. **2** represents a new polymorph of the compound *cis, fac*-[Ru(CH<sub>3</sub>CN)Cl<sub>2</sub>(dmsol)<sub>3</sub>] which was reported by Hall *et al.* in 2004<sup>30</sup>. The Ru-S bond distances in **1-3** [2.241(2)-2.2969(16) Å] is within the range reported for other ruthenium dmsol complexes.<sup>27</sup> Crystal packing in **1**, **2** and **3** is stabilised by intramolecular N-H...Cl, N-H...O, N-H...F, C-H...O, C-H...N, C-H...Cl and C-H...F H-bonding interactions.

### Catalytic Performances for the hydration of nitriles into amides

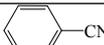
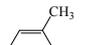
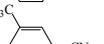
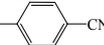
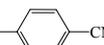
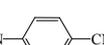
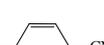
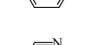
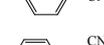
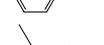
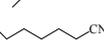
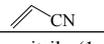
The ability of complexes **1-3** to promote the catalytic hydration of nitriles in water was evaluated at 60°C with 1 mmol nitrile in a culture tube under air as shown in Scheme 2.



**Scheme 2.** Ruthenium-catalysed hydration reaction

We first carried out the hydration of benzonitrile without complex **1-3** in water at 60°C for 24 h. We found that

**Table 1.** Ru-catalyzed hydration of nitriles to amides in water using complexes **1-3** as catalyst<sup>a</sup>

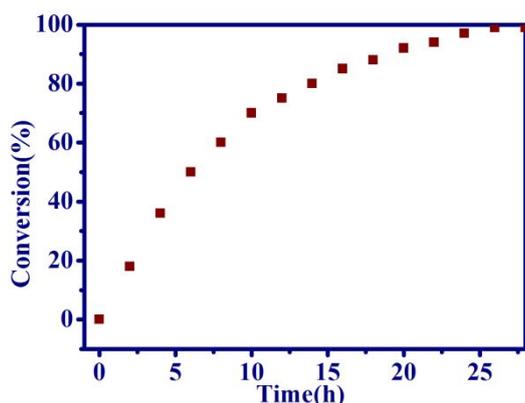
Entry	Substrate	Complex-1			Complex-2			Complex-3		
		Conversion (%) <sup>b</sup>	Isolated Yield (%) <sup>c</sup>	Selectivity (%) <sup>d</sup>	Conversion (%) <sup>b</sup>	Isolated Yield (%) <sup>c</sup>	Selectivity (%) <sup>d</sup>	Conversion (%) <sup>b</sup>	Isolated Yield (%) <sup>c</sup>	Selectivity (%) <sup>d</sup>
1.		64	60	>60	82	80	>80	99	95	>95
2.		62	59	>59	80	78	>78	98	92	>93
3.		65	61	>61	82	80	>80	99	90	>91
4.		62	61	>61	82	81	>81	99	90	>90
5.		58	60	>60	81	80	>80	99	92	>92
6.		56	58	>58	82	80	>80	99	91	>91
7.		63	64	>64	82	81	>81	99	88	>88
8.		60	61	>61	82	80	>80	99	93	>93
9.		62	60	>61	75	72	>72	82	75	>91
10.		64	59	>59	82	80	>80	99	85	>85
11.		63	60	>60	81	80	>80	99	86	>86
12.		59	60	>60	82	80	>80	99	90	>90
13.		64	62	>62	80	79	>79	99	88	>88

<sup>a</sup>Conditions: nitrile (1 mmol), complex **1-3** (5 mol%), H<sub>2</sub>O (3 mL), 60°C, in air. Time: 24 h reaction. <sup>b</sup>conversion determined by GCMS analysis. <sup>c</sup>Isolated by column chromatography. <sup>d</sup>Selectivity = (amide yield/substrate conversion) × 100.

benzonitrile was quantitatively recovered which indicated that no reaction occurred in the absence of complexes **1-3**. Under the same conditions as described above RuCl<sub>3</sub>·xH<sub>2</sub>O (5 mol%) provided a 50% conversion of benzonitrile to benzamide in 24h. Benzonitrile hydration by 5 mol% RuCl<sub>3</sub> had previously been reported to yield 54% benzamide after 24 h at 100°C.<sup>29</sup> We have also used [RuCl<sub>2</sub>(dmsO)<sub>4</sub>] (5 mol%) and [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] (5 mol%) as catalysts under the same conditions and found both were unable to catalyze the hydration of benzonitrile.<sup>23,32</sup> In contrast to the inactive [RuCl<sub>2</sub>(dmsO)<sub>4</sub>] and [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>], the hydration of benzonitrile catalyzed by [RuCl<sub>2</sub>(dmsO)<sub>2</sub>(NH<sub>3</sub>)(CH<sub>3</sub>CN)]/ [RuCl<sub>2</sub>(dmsO)<sub>3</sub>(CH<sub>3</sub>CN)]/ [RuCl<sub>2</sub>(dmsO)<sub>3</sub>(NH<sub>3</sub>)]·PF<sub>6</sub>·Cl gave 64-99% conversion of benzamide at 60°C after 24 h. Negligible formation of byproducts (e.g. carboxylic acid due to overhydrolysis) was

observed. The conversion of various nitriles to the corresponding amides was explored and the results are summarized in Table 1. All nitriles were efficiently converted to amides with 56-99% conversion in 24 h. After completion, the reactions were cooled to 0°C and, in most cases, the product amides crystallized out as white powders and were easily isolated in 58-95% yield by decantation. The isolated amides were characterized by GC-MS and <sup>1</sup>H & <sup>13</sup>C NMR spectroscopy. Substituted benzonitriles bearing electron-withdrawing groups (Table 1, entries 6-8) exhibited greater yield to amides than those with electron-donating groups (entries 2-5). Most probably, the presence of the electron withdrawing group makes the nitrile carbon more susceptible towards nucleophilic attack by an activated water molecule. This observation is in agreement with other catalyst systems<sup>33</sup>

although there have been exceptions reported.<sup>34</sup> The 2-methylbenzonitrile exhibited lower yield relative to 3- and 4-methylbenzonitrile (Table 1, entries 2-4), which can be attributed to steric hindrance at nitrile carbon in the 2-methylbenzonitrile due to -CH<sub>3</sub> moiety. This indicates nitrile activation by coordination to ruthenium may be necessary. These results are comparable to the previously reported for methyl-substituted benzonitriles.<sup>33b,35</sup> The hydration of 4-formylbenzonitrile led to 4-formylbenzamide in a 60-99% conversion in 24 h with an intact formyl moiety (entry 8). The coordinating ability of the pyridyl functionality reduces catalytic activity as hydration of 2-cyanopyridine to picolinamide resulted in only 62-82% conversion after 24 h (entry 9). [RuCl<sub>2</sub>(dmsO)<sub>2</sub>(NH<sub>3</sub>)(CH<sub>3</sub>CN)]/[RuCl<sub>2</sub>(dmsO)<sub>3</sub>(CH<sub>3</sub>CN)]/[RuCl<sub>2</sub>(dmsO)<sub>3</sub>(NH<sub>3</sub>)]·PF<sub>6</sub>·Cl were found to be an effective hydration catalyst for the deactivated aliphatic nitriles (Table 1, entries 11-13). The scope of this system was further examined with 4-Methylbenzyl cyanide, pivalonitrile and acrylonitrile. 4-Methylbenzyl cyanide was transformed into amide with 59-85% yield in 24 h (entry 10). The sterically bulky pivalonitrile was converted into pivalamide with 60-86% yield in 24 h (entry 11). We have noted the resistance of tertiary nitriles toward hydrolysis.<sup>36</sup> The industrially important acrylonitrile was converted into acrylamide with 62-88% yield in 24 h without any polymerized or hydrolysis byproducts (Table 1, entry 13). The catalytic activity decreased in the following order: **3** > **2** > **1**. For all the nitrile hydrations studied, the corresponding amides were the only product observed without any byproducts. Thus, the scope of this catalytic system described here is tolerated with hydroxyl, nitro, bromo, formyl, pyridyl, benzyl, alkyl, and olefinic functional groups, which establishes a wide synthetic scope. No induction period was observed in a kinetics plot of the hydration of benzonitrile by [RuCl<sub>2</sub>(dmsO)<sub>3</sub>(NH<sub>3</sub>)]·PF<sub>6</sub>·Cl in water (Fig. 5). Free dmsO was observed in solution while monitoring the reaction by <sup>1</sup>H NMR spectroscopy (see Fig. S5 to Fig. S7, ESI<sup>†</sup>).



**Fig. 5.** Kinetics for the hydration of benzonitrile using [RuCl<sub>2</sub>(dmsO)<sub>3</sub>(NH<sub>3</sub>)]·PF<sub>6</sub>·Cl. Conversions were determined by GC-MS with each data point a separate reaction under identical conditions: benzonitrile (1 mmol), [RuCl<sub>2</sub>(dmsO)<sub>3</sub>(NH<sub>3</sub>)]·PF<sub>6</sub>·Cl (5 mol%), H<sub>2</sub>O (3 mL), 60°C, in air.

**Table 2.** Effect of reduced catalyst loading on the hydration of benzonitrile catalyzed by [RuCl<sub>2</sub>(dmsO)<sub>3</sub>(NH<sub>3</sub>)]·PF<sub>6</sub>·Cl<sup>a</sup>

Entry	Catalyst (mol%)	Time (h)	Yield <sup>b</sup> (%)	TON <sup>c</sup>	TOF <sup>d</sup> (h <sup>-1</sup> )
1.	5	24	90	18	0.75
2.	1	24	92	92	3.83
3.	0.1	24	94	940	39.16
4.	0.01	24	96	9600	400
5.	0.001	24	99	99000	4125
6.	0.0001	24	99	990000	41250

<sup>a</sup>Conditions: nitrile (1 mmol), H<sub>2</sub>O (3 mL), 60°C, in air. <sup>b</sup>Isolated by column chromatography. <sup>c</sup>TON (mol product)/(mol catalyst). <sup>d</sup>TOF (mol product)/(mol catalyst) h<sup>-1</sup>.

This suggests that formation of the catalytically active species may involve dmsO dissociation, presumably followed by nitrile coordination.<sup>21</sup> From the mechanistic point of view, coordination of the nitrile to the ruthenium centre is a prerequisite condition for nitrile hydration. In this way, the CN bond is activated towards the nucleophilic addition of water *via* a metal-ligand cooperative mechanism thus enhancing the reaction rate has been proposed. The presence of a NH<sub>3</sub> ligand is crucial for the hydration reaction to occur. The NH<sub>3</sub> ligand coordinated to Ru could interact with water molecules by H-bonding facilitating the attack to the nitrile (see Fig. S8, ESI<sup>†</sup>). The durability of [RuCl<sub>2</sub>(dmsO)<sub>3</sub>(NH<sub>3</sub>)]·PF<sub>6</sub>·Cl was evaluated by reducing the catalyst loading (Table 2). We examined catalyst loading down to 0.0001 mol% for the hydration of benzonitrile. Turnover numbers (TONs) up to 990000 (entry 6, Table 2) were obtained, which are among the highest reported to date.

**Table 3.** Effect of dilution on the hydration of benzonitrile at 1 mol% catalyst loading<sup>a</sup>.

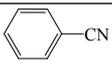
Entry	H <sub>2</sub> O(mL)	Nitrile(M)	Yield(%) <sup>b</sup>		
			2h	8h	24h
1.	1	1	20	70	99
2.	3	0.50	42	92	99
3.	5	0.25	45	96	99

<sup>a</sup>Conditions: nitrile (1 mmol), complex **3** (1 mol%), 60°C, in air. <sup>b</sup>Isolated by column chromatography.

We have also studied the effect of dilution on the hydration reaction. We observed that the rate of hydration was found to increase with an increase in the volume of water (i.e. dilution) possibly indication of substrate/product inhibition at higher concentrations as shown in Table 3. Better catalytic performance (higher TOF) has been reported for other ruthenium complexes at lower concentration of the catalyst.<sup>13,37</sup> We have further studied the evidence of the robust nature of the catalyst which was obtained upon storing an aqueous solution of [RuCl<sub>2</sub>(dmsO)<sub>3</sub>(NH<sub>3</sub>)]·PF<sub>6</sub>·Cl under air for four weeks at room temperature (see Fig. S9, ESI<sup>†</sup>). The hydration of benzonitrile was carried out with the stored aqueous solution of [RuCl<sub>2</sub>(dmsO)<sub>3</sub>(NH<sub>3</sub>)]·PF<sub>6</sub>·Cl (1 mol% loading) resulted in a 96% yield after 24 h compared to 99% by freshly-prepared catalyst in water. The ability to store aqueous solutions of [RuCl<sub>2</sub>(dmsO)<sub>3</sub>(NH<sub>3</sub>)]·PF<sub>6</sub>·Cl encouraged us to further explore the reusability of the catalyst through recycling experiments with benzonitrile as shown in Table 4. After 24 h the reaction was cooled overnight and the aqueous supernatant containing the catalyst was carefully transferred to another reaction tube followed by addition of fresh nitrile. The precipitated amide

product was collected and washed with cold water. Further purity was determined by GC-MS,  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy. The isolated yields in Table 4 were obtained by decantation; maximized isolated yields (99%) can be obtained by extraction with an organic solvent (Table 4, run 1).

**Table 4.** Recycling experiments with  $[\text{RuCl}_2(\text{dmsO})_3(\text{NH}_3)]\cdot\text{PF}_6\cdot\text{Cl}$  under aqueous conditions<sup>a</sup>

Substrate	Recycling experiment <sup>b</sup>							
	1	2	3	4	5	6	7	8
	99	99	99	99	99	99	97	95

<sup>a</sup>Conditions: nitrile (1 mmol),  $[\text{RuCl}_2(\text{dmsO})_3(\text{NH}_3)]\cdot\text{PF}_6\cdot\text{Cl}$  (5 mol%),  $\text{H}_2\text{O}$  (3 mL),  $60^\circ\text{C}$ , 24 h, in air. <sup>b</sup>isolated yields.

Recycling was carried out at least seven times without significant loss of the catalytic activity or selectivity in the case of benzonitrile. To verify the practicability of this reaction system, a gram-scale hydration was carried out using benzonitrile (16 mmol, 1.649 g),  $[\text{RuCl}_2(\text{dmsO})_3(\text{NH}_3)]\cdot\text{PF}_6\cdot\text{Cl}$  (0.0016 mol%) and  $\text{H}_2\text{O}$  (48 mL) at  $60^\circ\text{C}$  for 24 h gave 99% isolated yield of benzamide (1.917 g).

## Conclusions

In conclusion, we have described new Ru(II) and (IV)-dmsO complex capable of catalysing the selective hydration of a large number of organonitriles in water under milder conditions. Advantages of this catalytic system discussed here include easy catalyst preparation, simple reaction setup, and the use of green solvent (water). The catalyst is robust and highly recyclable under atmospheric conditions. Isolation of many amides by decantation from water largely circumvents the use of organic solvents, even in the workup steps. The amide synthesis by hydration of nitriles using  $[\text{RuCl}_2(\text{dmsO})_3(\text{NH}_3)]\cdot\text{PF}_6\cdot\text{Cl}$  in water is simple, practical and environmental friendly.

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## Notes and references

- 1 P. Anastas, J. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, New York, 1998.
- 2 R.A. Sheldon, *Green Chem.*, 2005, **7**, 267.
- 3 (a) D.J. Adams, P.J. Dyson, S.J. Tavener, *Chemistry in Alternative Reaction Media*, Wiley, 2004; (b) S. Liu, J. Xiao, *J. Mol. Catal. A: Chem.*, 2007, **270**, 1; (c) C. Reichardt, *Org. Process Res. Dev.*, 2007, **11**, 105.

- 4 (a) U.M. Lindström, *Organic Reactions in Water*, Blackwell, Oxford, 2007; (b) C. J. Li, *Chem. Rev.*, 1993, **93**, 2023; (c) C. J. Li, *Chem. Rev.*, 2005, **105**, 3095; (c) A. Chanda, V.V. Fokin, *Chem. Rev.*, 2009, **109**, 725.
- 5 H.C. Hailes, *Org. Process Res. Dev.*, 2007, **11**, 114.
- 6 L. Chen, C.-J. Li, *Adv. Synth. Catal.*, 2006, **348**, 1459.
- 7 V.Y. Kukushkin, A.J.L. Pombeiro, *Chem. Rev.*, 2002, **102**, 1771.
- 8 P.K. Mascharak, *Coord. Chem. Rev.*, 2002, **225**, 201.
- 9 V.Y. Kukushkin, A.J.L. Pombeiro, *Inorg. Chim. Acta*, 2005, **358**, 1.
- 10 A. Goto, K. Endo, S. Saito, *Angew. Chem., Int. Ed.*, 2008, **47**, 3607.
- 11 (a) A.W. Parkins, *Platinum Met. Rev.*, 1996, **40**, 169; (b) T.J. Ahmed, S.M.M. Knapp, D.R. Tyler, *Coord. Chem. Rev.*, 2011, **255**, 949.
- 12 (a) M. Martin, H. Horváth, E. Sola, Á. Kathó, F. Joó, *Organometallics* 2009, **28**, 561; (b) S.-I. Murahashi, S. Sasao, E. Saito, T. Naota, *J. Org. Chem.*, 1992, **57**, 2521; (c) S.-I. Murahashi, S. Sasao, E. Saito, T. Naota, *Tetrahedron*, 1993, **49**, 8805; (d) S.-I. Murahashi, H. Takaya, *Acc. Chem. Res.*, 2000, **33**, 225; (e) W.-G. Jia, S. Ling, S.-J. Fang, E.-H. Sheng, *Polyhedron*, 2017, **138**, 1.
- 13 T. Oshiki, H. Yamashita, K. Sawada, M. Utsunomiya, K. Takahashi, K. Takai, *Organometallics*, 2005, **24**, 6287.
- 14 R. García-Álvarez, J. Díez, P. Crochet, V. Cadierno, *Organometallics* 2010, **29**, 3955.
- 15 V. Cadierno, J. Francos, J. Gimeno, *Chem. Eur. J.* 2008, **14**, 6601.
- 16 R. García-Álvarez, J. Díez, P. Crochet, V. Cadierno, *Organometallics* 2011, **30**, 5442.
- 17 R. García-Álvarez, J. Francos, P. Crochet, V. Cadierno, *Tetrahedron Lett.* 2011, **52**, 4218.
- 18 V. Cadierno, J. Díez, J. Francos, J. Gimeno, *Chem. Eur. J.* 2010, **16**, 9808.
- 19 R. García-Álvarez, M. Zablocka, P. Crochet, C. Duhayon, J.-P. Majoral, V. Cadierno, *Green Chem.* 2013, **15**, 2447.
- 20 (a) R. García-Álvarez, J. Díez, P. Crochet, V. Cadierno, *Organometallics*, 2010, **29**, 3955; (b) R. García-Álvarez, P. Crochet, V. Cadierno, *Green Chem.*, 2013, **15**, 46; (c) Í. Ferrer, X. Fontrodona, M. Rodríguez and I. Romero, *Dalton Trans.* 2016, **45**, 3163; (d) R. González-Fernández, P. Crochet, V. Cadierno, M.I. Menéndez, R. López, *Chem. Eur. J.* 2017, **23**, 15210; (e) M.K. Rong, K. van Duin, T. van Dijk, J.J.M. de Pater, B.J. Deelman, M. Nieger, A.W. Ehlers, J.C. Slootweg, K. Lammertsma, *Organometallics* 2017, **36**, 1079; (f) W.L. Ounkham, J.A. Weeden, and B.J. Frost, *Chem. Eur. J.* 2019, **25**, 10013; (g) E. Tomás-Mendivil, F.J. Suárez, J. Díez, V. Cadierno, *Chem. Commun.*, 2014, **50**, 9661; (h) E. Tomás-Mendivil, J. Francos, R. González-Fernández, P.J. González-Liste, J. Borge and V. Cadierno, *Dalton Trans.*, 2016, **45**, 13590; (i) R. García-Álvarez, J. Francos, E. Tomás-Mendivil, P. Crochet, V. Cadierno, *Journal of Organometallic Chemistry*, 2014, **771**, 93.
- 21 Í. Ferrer, J. Rich, X. Fontrodona, M. Rodríguez, I. Romero, *Dalton Trans.*, 2013, **42**, 13461
- 22 E. Manrique, I. Ferrer, C. Lu, X. Fontrodona, M. Rodríguez, I. Romero, *Inorg. Chem.* 2019, **58**, 8460.
- 23 E. Bolyog-Nagy, A. Udvardy, F. Joó, Á. Kathó, *Tetrahedron Letters* 2014, **55**, 3615.
- 24 E. Alessio, G. Mestroni, G. Nardin, W.M. Attia, M. Calligaris, G. Sava, S. Zorzet, *Inorg. Chem.* 1988, **27**, 4099.
- 25 (a) G.M. Sheldrick, SHELX-97; Programme for Refinement of Crystal Structures, University of Gottingen, Gottingen, Germany, 1997; (b) G.M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2007, **64**, 112.

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2  
3 26 (a) P. Van der Sluis and A.L. Spek, *Acta Crystallogr.*, Sect.  
4 A: *Fundam. Crystallogr.*, 1990, **46**, 194; (b) PLATON, A.L.  
5 Spek, *Acta Cryst.* 1990, **46A**, C34.
- 6 27 (a) I. Bratsos, B. Serli, E. Zangrando, N. Katsaros, E. Alessio,  
7 *Inorg. Chem.* 2007, **46**, 975; (b) R. Ziessel, V. Grosshenny,  
8 M. Hissler, C. Stroh, *Inorg. Chem.* 2004, **43**, 4262; (c) C.  
9 Sens, M. Rodríguez, I. Romero, A. Llobet, T. Parella, B.P.  
10 Sullivan, J. Benet-Buchholz, *Inorg. Chem.* 2003, **42**, 2040;  
11 (d) E. Reisner, V.B. Arion, A. Ruffínska, I. Chiorescu, W.F.  
12 Schmid, B.K. Keppler, *Dalton Trans.* 2005, 2355; (e) J.  
13 Mola, I. Romero, M. Rodríguez, F. Bozoglian, A. Poater, M.  
14 Solá, T. Parella, J. Benet-Buchholz, X. Fontrodona, A.  
15 Llobet, *Inorg. Chem.* 2007, **46**, 10707.
- 16 28 J. Mola, I. Romero, M. Rodríguez, F. Bozoglian, A. Poater,  
17 Miquel Solá, T. Parella, J. Benet-Buchholz, X. Fontrodona,  
18 A. Llobet, *Inorg. Chem.* 2007, **46**, 10707.
- 19 29 E. Alessio, B. Milani, G. Mestroni, M. Calligaris, P.  
20 Faleschini, W.M. Attia, *Inorg. Chim. Acta*, 1990, 177, 255.
- 21 30 P.M.T. Piggot, L.A. Hall, A.J.P. White, D.J. Williams,  
22 *Inorganica Chimica Acta* 2004, **357**, 250.
- 23 31 W.-C. Lee, B.J. Frost, *Green Chem.*, 2012, **14**, 62.
- 24 32 (a) C.-J. Li, D. Wang, D.-L. Chen, *J. Am. Chem. Soc.*, 1995,  
25 **117**, 12867; (b) D. Wang, D. Chen, J.X. Habelman, D.-L.  
26 Chen, *Tetrahedron*, 1998, **54**, 5129.
- 27 33 (a) S.E. García-Garrido, J. Francos, V. Cadierno, J.-M.  
28 Basset, V. Polshettiwar, *ChemSusChem*, 2011, **4**, 104; (b) R.  
29 Ramón, N. Marion, S.P. Nolan, *Chem.-Eur. J.*, 2009, **15**,  
30 8695.
- 31 34 (a) K. Yamaguchi, M. Matsushita, N. Mizuno, *Angew.*  
32 *Chem., Int. Ed.*, 2004, **43**, 1576; (b) A.Y. Kim, H.S. Bae, S.  
33 Park, S. Park, K.H. Park, *Catal. Lett.*, 2011, **141**, 685.
- 34 35 (a) M. Muranaka, I. Hyodo, W. Okumura, T. Oshiki, *Catal.*  
35 *Today*, 2011, **164**, 552; (b) A. Goto, K. Endo, S. Saito,  
36 *Angew. Chem., Int. Ed.*, 2008, **47**, 3607.
- 37 36 X.-b. Jiang, A.J. Minnaard, B.L. Feringa, J.G. de Vries, *J.*  
38 *Org. Chem.*, 2004, **69**, 2327.
- 39 37 A. Cavarzan, A. Scarso, G. Strukul, *Green Chem.*, 2010, **12**,  
40 790.
- 41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
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