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Synthesis and Catalytic Water Oxidation Activities of Ruthenium Complexes Containing Neutral Ligands

Yunhua Xu,[a] Lele Duan,[a] Torbjörn Åkermark,[b] Lianpeng Tong,[a] Bao-Lin Lee,[c] Rong Zhang,[d] Björn Åkermark,[c] and Licheng Sun*[a, d]

Abstract: Two dinuclear and one mononuclear ruthenium complexes containing neutral polypyridyl ligands have been synthesised as pre-water oxidation catalysts and characterised by ^{1}H and ^{13}C NMR spectroscopy and ESI-MS. Their catalytic water oxidation properties in the presence of [Ce$(NH_4)_2(NO_3)_6$] (Ce^{IV}) as oxidant at pH 1.0 have been investigated. At low concentrations of Ce^{IV} (5 mM), high turnover numbers of up to 4500 have been achieved. An ^{18}O-labelling experiment established that both O atoms in the evolved O_2 originate from water. Combined electrochemical study and electrospray ionisation mass spectrometric analysis suggest that ligand exchange between coordinated 4-picoline and free water produces Ru aquo species as the real water oxidation catalysts.

Keywords: homogeneous catalysis · isotopic labeling · neutral ligands · ruthenium · water oxidation

Introduction

As global energy demand continues to increase, the development of sustainable and environmentally friendly energy resources has become a big challenge for scientists. Solar energy is believed to be one of the most promising ways to solve this problem.[1] Through light-driven water splitting, for example, solar energy can be converted into dihydrogen—a clean and valuable fuel. The most challenging step in this artificial photosynthesis process has been found to be water oxidation, now intensely studied by many research groups. Considerable efforts have been made to develop synthetic analogues of the oxygen-evolving complex (OEC) in photosystem II (PSII), which contains a Mn_4Ca cluster as the water oxidation catalyst.[2] These model systems have mainly been focused either on manganese-based complexes,[3–7] which mimics nature's preference, or on ruthenium-based complexes,[4–24] although other metal complexes (Co, Ir, Fe) have also been investigated.[25–29] Although only a very few of the manganese complexes that have been synthesised have shown moderate to low catalytic activity for water oxidation,[30–34] many ruthenium complexes with high catalytic activities have been developed.[4–24] As early as the 1980s, Meyer and co-workers reported a few dinuclear ruthenium complexes (such as the "blue dimer" **A**, Scheme 1) as water oxidation catalysts,[35] in 2004 Llobet and co-workers described a new type of dinuclear complex (**B**, Scheme 1) that contains no Ru-O-Ru motif but is still active for water oxidation,[11] whereas in 2005 Thummel and co-workers presented a series of dinuclear ruthenium complexes (such as **C**, Scheme 1) capable of catalysing water oxidation.[12] In 2008, Sartorel and Hill independently reported a tetraruthenium-oxo oxygen-evolving catalyst containing all-inorganic POM ligands.[16,17]

Several research groups have recently also reported that mononuclear ruthenium complexes can efficiently catalyse water oxidation.[14,36] Negatively charged ligands can lower the oxidation potentials of metal complexes and thus stabilise the high oxidation states of the metal ions,[37] and so we have employed carboxylate ligands to synthesise highly efficient water oxidation catalysts. We have previously reported dinuclear (**D** and **E**, Figure 1)[20–22] and mononuclear ruthenium complexes,[18,19,23] which indeed promise high activities. In addition to manganese- and ruthenium-based complexes, in 2008 Bernhard and co-workers reported iridium-based aquo complexes that can also catalyse homogeneous water oxidation in the presence of $Ce(NH_4)_2(NO_3)_6$ (Ce^{IV}) as oxidant with turnover numbers (TONs) of over 2000.[27]

Although negatively charged carboxylate ligands can usefully improve the catalytic properties of metal complexes,

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[a] Dr. Y. Xu, L. Duan, L. Tong, Prof. L. Sun
Department of Chemistry
School of Chemical Science and Engineering
Royal Institute of Technology (KTH)
100 44 Stockholm (Sweden)
Fax: (+46) 8-791-2333
E-mail: lichengs@kth.se

[b] Dr. T. Åkermark
Department of Materials and Environmental Chemistry
Arrhenius Laboratory, Stockholm University,
106 91 Stockholm (Sweden)

[c] B.-L. Lee, Prof. B. Åkermark
Department of Organic Chemistry, Arrhenius Laboratory
Stockholm University, 106 91 Stockholm (Sweden)

[d] Dr. R. Zhang, Prof. L. Sun
State Key Laboratory of Fine Chemicals
DUT-KTH Joint Education
and Research Centre on Molecular Devices
Dalian University of Technology (DUT)
Dalian 11602 (P.R. China)

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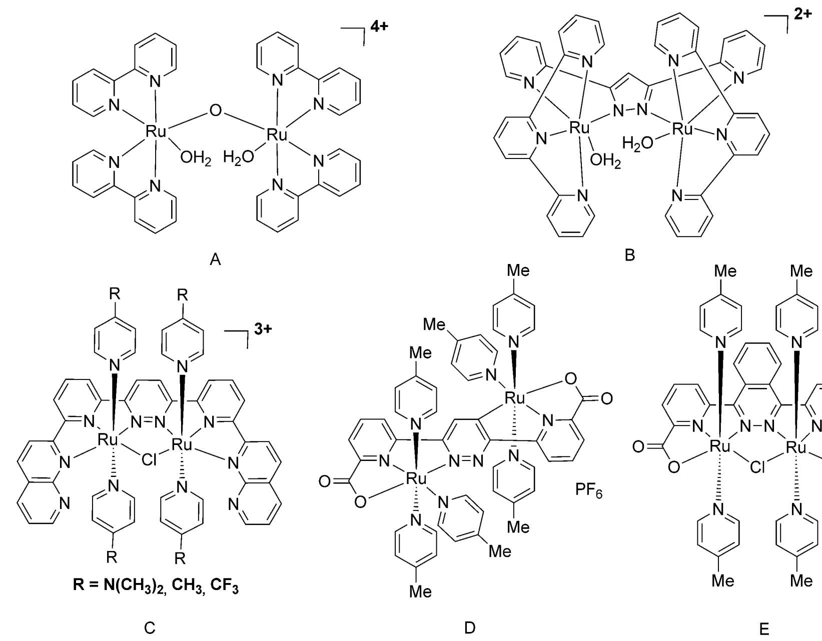


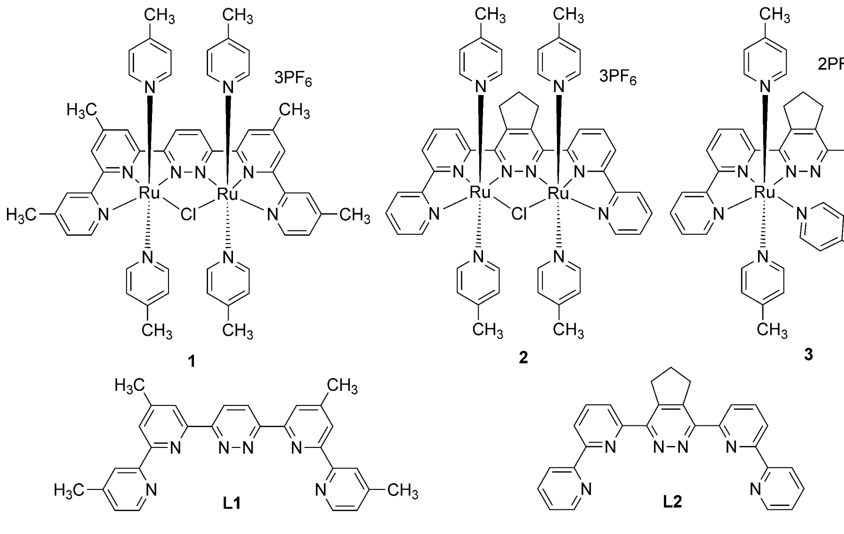
Scheme 1. Structures of some reported Ru-based water oxidation catalysts.

they have some drawbacks. When the carboxylate ligands are coordinated with manganese, for example, insoluble oligomers or polymers are easily formed, giving rise to serious problems for homogeneous water oxidation. In this respect, improvement of the catalytic activities of metal complexes containing neutral ligands is of interest as well. In the case of the complexes **C**, electron-donating groups at the 4-pyridyl positions have been shown to enhance the catalytic activities.[12] To enhance the electron-donating ability of its polypyridyl bridging ligand, we modified Thummel's ligands (**C**) by removing the uncoordinated pyridyl motifs and introducing alkyl groups on the equatorial polypyridyl ligand. Here we present several ruthenium complexes (complexes **1**–**3**, Scheme 2) containing neutral polypyridyl ligands and explore their catalytic activities in the presence of Ce^{IV} as sacrificial electron acceptor. As expected, we gained enhanced catalytic activity relative to the complexes **C**.

Results and Discussion

Synthesis and characterisation: The ligand **L1** was prepared by the route shown in Scheme 3, from 4,4′-dimethyl-2,2′-bipyridine (**4**) as the starting material. The compound **4** was oxidised with *meta*-chloroperbenzoic acid (*m*-CPBA) to form the N-oxide **5**, which was further treated with trimethylsilyl cyanide in the presence of carbamoyl chloride to yield 6-cyano-2,2′-bipyridine (**6**).[38] This was subsequently treated with hydrazine in ethanol to form the dihydro base **7**, which was further oxidised with nitric acid in acetic acid to afford the tetrazine **8** as a pink solid.[39] Bubbling of acetylene through a solution of **8** in DMF at reflux provided the bis-tridentate ligand 3,6-bis-(4,4′-dimethyl-2,2′-bipyrid-6-yl)pyridazine (**L1**) as a white solid.[39]

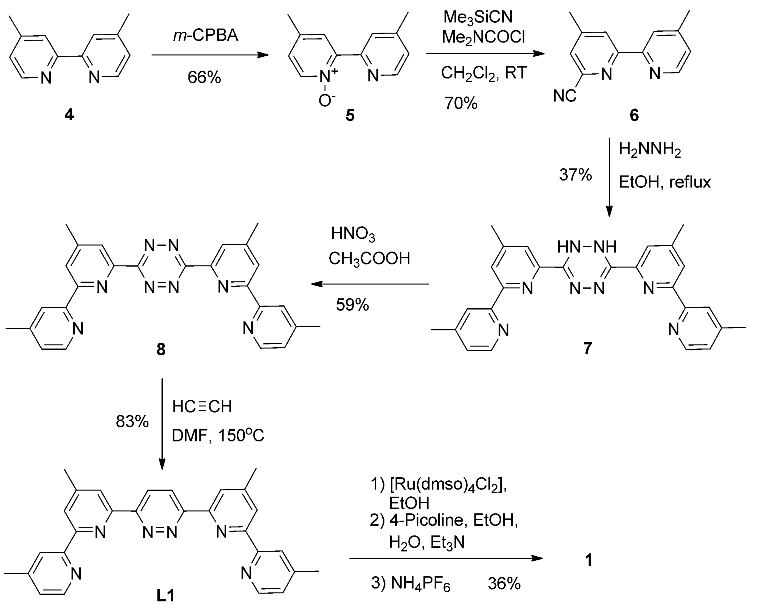
The synthesis of **L2** is shown in Scheme 4. The compound **11** could be obtained in a good yield by a procedure similar to that described above. A reaction between **11** and cyclopentanone at 110 °C in toluene in the presence of morpholine and silica gel afforded the ligand **L2** in a quantitative yield.[40]



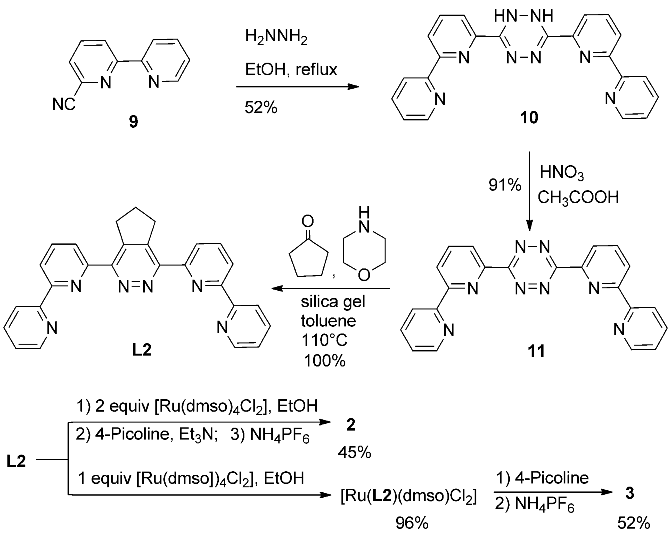
Scheme 2. Molecular structures of the complexes **1**–**3** and the ligands **L1** and **L2**.

The syntheses of the complexes **1** and **2** were carried out by treatment of the ligands with *cis*-Ru(dmso)$_4$Cl$_2$ in ethanol, followed by addition of excess 4-methylpyridine in the presence of triethylamine and LiCl (see also Schemes 3 and 4). Ion exchange with NH$_4$PF$_6$ gave precipitates, which were purified by column chromatography to afford the desired products in 35–45 % yields.

The complex **3** was prepared by treatment of the ligand **L2** with *cis*-[Ru(dmso)$_4$Cl$_2$] in ethanol to give a black precipitate. This precipitate was shown to be [Ru(**L2**)(dmso)Cl$_2$], although the **L2**/Ru(dmso)$_4$Cl$_2$



Scheme 3. Synthesis of the complex **1**.



Scheme 4. Syntheses of the complexes **2** and **3**.

ratio in the reaction mixture had been 1:2. This intermediate was further heated at reflux with excess 4-picoline in an ethanol/water mixture (9:1), followed by purification to afford the complex **3** in 52 % yield.

All complexes and compounds except for the tetrazines **8** and **11** were characterised by NMR spectroscopy. The structures of the complexes **1**–**3** were also confirmed by ESI-MS data. All ^{1}H and ^{13}C NMR and mass spectral data are consistent with both **1** and **2** having symmetric structures, each containing a μ-Cl bridge, similar to the dinuclear ruthenium complexes reported by Thummel and co-workers.[12] In the mass spectrum of **1**, the peak corresponding to $[M{-}3PF_6]^{3+}$ was found at $m/z = 351.7380$ (calcd: 351.7384). For the complex **2**, peaks for $[M{-}3PF_6]^{3+}$, $[M{-}2PF_6]^{2+}$ and $[M{-}PF_6]^{+}$ were observed at $m/z = 346.16$, 592.06 and 1328.93, respectively.

Absorption spectroscopy: UV/Vis spectra of the complexes **1**–**3** in acetonitrile are shown in Figure 1 and the electronic absorption data are summarised in Table 1.

The complex **1** has an electronic spectrum similar to those reported by Thummel for the complexes **C**.[12] In the UV region, there are three absorption maxima at 275, 310 and 345 nm assigned to ligand-centred (LC) π–π* transitions. In the visible region, three relatively weak absorption maxima were observed at 437, 483 and 567 nm. They are assigned to metal-to-ligand charge transfer (MLCT) transitions involving electron promotions from the Ru d orbitals to the ligand

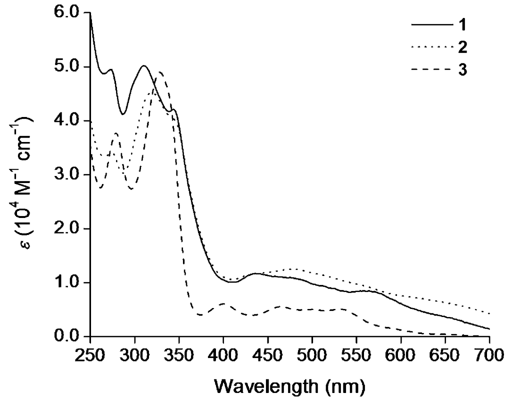


Figure 1. UV/Vis spectra of the complexes **1**–**3** in acetonitrile.

Table 1. Electronic absorption and electrochemical data for the complexes **1**–**3**.

Complex	λ_{max} [nm (ε/10^4 $M^{-1}cm^{-1}$)][a]	$E_{1/2}$ [V][b] (ΔE_p [mV])[c]
1	275 (4.94), 310 (4.98), 345 (4.16), 437 (1.14), 483 (1.09), 567 (0.84)	−0.98 (57), −0.47 (59), 1.46 (61), 1.89 (47)
2	276 (3.35), 315 (4.47), 345 (4.00), 436 (1.16), 479 (1.23), 639 (0.67)	−0.96 (80), −0.50 (92), 1.44 (93), 1.95 (80)
3	278 (3.75), 327 (4.85), 400 (0.61), 463 (0.54), 536 (0.46)	−0.85 (78), 1.46 (92)

[a] In CH_3CN solution. [b] Versus NHE. [c] $\nu = 0.1\ Vs^{-1}$; $\Delta E_p = E_{pa} - E_{pc}$.

π* orbitals. The complex **2** shows similar absorption to the complex **1** in the MLCT bands, but has a much smaller extinction coefficient than **1** in the 250–300 nm region. In the UV region the monomeric complex **3** displays absorption strength similar to that of the complex **2** but much weaker absorption than the complexes **1** and **2** in the visible region.

Electrochemistry: The electrochemistry of the complexes **1**–**3** was studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The electrochemical data are also given in Table 1. All potentials reported here are versus NHE.

In acetonitrile: The CV of **1** (Figure 2a) in dry acetonitrile has two reversible one-electron oxidation waves at $E_{1/2}=$ 1.46 and 1.89 V, which is similar to the values reported for the related complex **C** (Figure 2, $R=CH_3$).[12] They are assigned to the oxidations of the $Ru_2^{II,II}$ to $Ru_2^{II,III}$ and $Ru_2^{II,III}$ to $Ru_2^{III,III}$, respectively. In addition to these two oxidation peaks, two reversible one-electron reduction waves were also observed at $E_{1/2}=-0.47$ and -0.98 V. These are assigned to the ligand-based reductions of the complex. Additional ligand-based reduction could also be observed at $E_{pk}=-1.60$ V (DPV peak potential) as shown in Figure 2b.

For the complex **2**, the oxidation of the $Ru_2^{II,II}$ to $Ru_2^{II,III}$ occurs at $E_{1/2}=1.44$ V (Figure 3a), 20 mV lower than in the case of **1**, whereas the oxidation of $Ru_2^{II,III}$ to $Ru_2^{III,III}$ is at $E_{1/2}=1.95$ V, 60 mV higher than in the case of **1**. The ligand-based reductions of **2** were observed at $E_{1/2}=-0.50$ and -0.96 V (see also Figure 3a). The complex **3** shows that a $Ru^{III/II}$ redox couple arises at $E_{1/2}=1.46$ V and a ligand-based reduction at $E_{1/2}=-0.85$ V (Figure 3b).

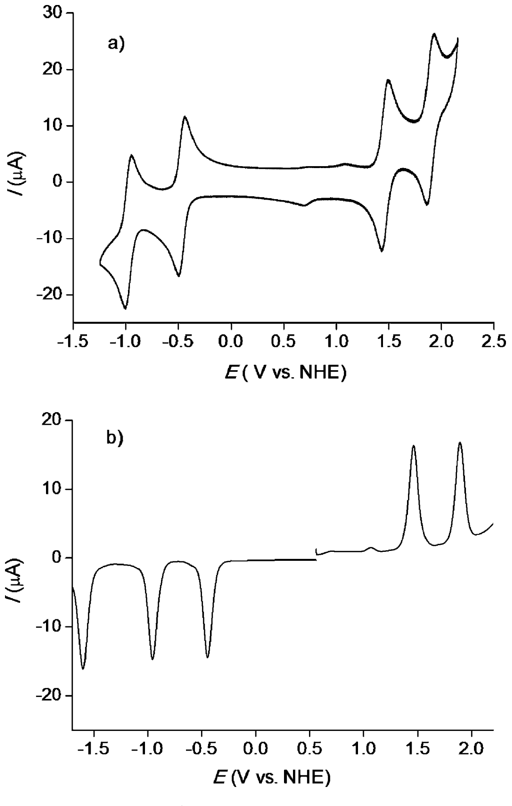


Figure 2. a) CV (υ = 0.1 V s^{-1}) and b) DPV of **1** (1 mM) in dry acetonitrile with Bu_4NPF_6 (0.1 M) as the supporting electrolyte, glassy carbon disk as the working electrode and $Ag/AgNO_3$ as the reference electrode.

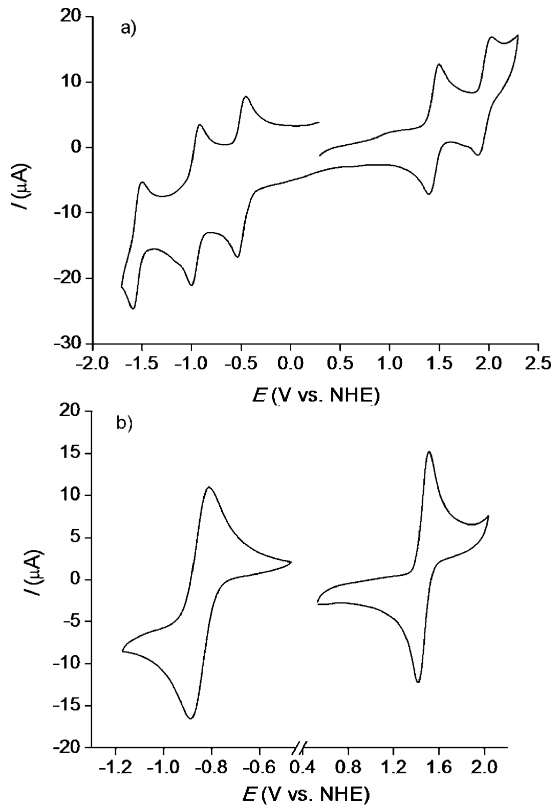


Figure 3. CVs (υ = 0.1 V s^{-1}) a) of **2** (1 mM), and b) of **3** (1 mM) in dry acetonitrile with Bu_4NPF_6 (0.1 M) as the supporting electrolyte, glassy carbon disk as the working electrode and $Ag/AgNO_3$ as the reference electrode.

Notably, both the first and the second oxidation potentials of the dimeric complexes **1** and **2** are about 0.5 V higher than the corresponding ones of the complex **E**, which has a similar structure but contains negatively charged ligands.[22]

The electrochemical behaviour of the dinuclear ruthenium complexes in the presence of a small amount of water was also studied. When water (3 %, v/v) was added to the acetonitrile solution of **1**, the CV (Figure 4, solid curve) in the potential range below 2.0 V displayed well-defined reversible redox waves similar to those seen in the dry acetonitrile. Above about 2.2 V, a potential slightly higher than the oxidation of $Ru_2^{II,III}$ to $Ru_2^{III,III}$, however, a very large irreversible oxidation peak was observed, clearly indicating catalytic water oxidation by the complex **1**.

In aqueous solution (pH 1): In aqueous CF_3SO_3H (pH 1.0), only one redox couple for each complex was observed in the 0.15–1.65 V region (Figure 5). The redox couples at $E_{1/2}=$ 1.23, 1.21 are related to $Ru^{III,II/II,II}$ in **1** and **2**, respectively. These values are higher than those for the complexes **D** and **E**.[20,22] The $Ru^{III/II}$ redox couple of **3** was detected at $E_{1/2}=$ 1.23 V.

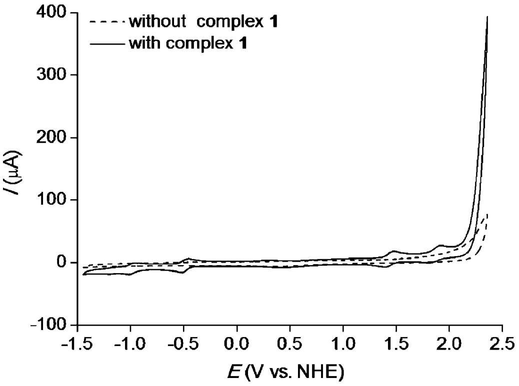


Figure 4. CV ($\upsilon = 0.1\ \mathrm{V\,s^{-1}}$) of **1** (1 mM) in an acetonitrile/water (100:3) mixture with Bu_4NPF_6 (0.1 M) as the supporting electrolyte, glassy carbon disk as the working electrode and $Ag/AgNO_3$ as the reference electrode.

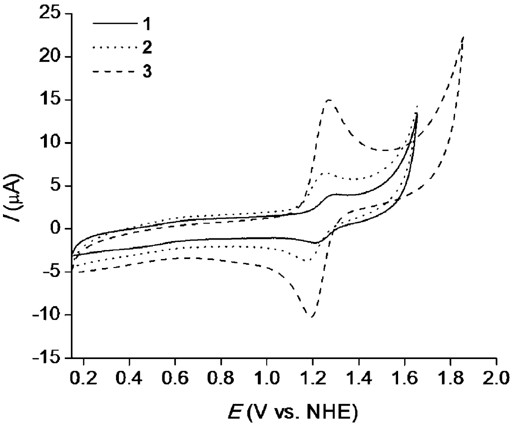


Figure 5. CVs ($\upsilon = 0.1\ \mathrm{V\,s^{-1}}$) of the complexes **1** (saturated), **2** (saturated) and **3** (1 mM) in aqueous CF_3SO_3H (pH 1.0) with glassy carbon disk as the working electrode and Ag/AgCl as the reference electrode.

Catalytic activity in water oxidation: The catalytic activities of the complexes **1**–**3** in water oxidation were investigated with use of Ce^{IV} as oxidant in aqueous CF_3SO_3H (pH 1.0) solutions [Eq. (1)].

$$4Ce^{IV} + 2H_2O \xrightarrow{catalyst} 4Ce^{III} + O_2 + 4H^+ \quad (1)$$

Evolved oxygen in the headspace of the reaction flask was measured by gas chromatography (GC) and the reaction kinetics were monitored with an oxygen sensor. Figure 6 shows the kinetics of oxygen evolution catalysed by the complexes **1**–**3**. When a solution of the complex **1** or **2** in acetonitrile was added to a deaerated water solution (pH 1.0, adjusted with CF_3SO_3H) containing Ce^{IV} (330 mM), dioxygen gas was produced immediately. In the absence of catalysts, no oxygen evolution was found under otherwise the same conditions. The initial turnover frequencies (TOFs) are $0.09\ \mathrm{s^{-1}}$ for **1** and $0.10\ \mathrm{s^{-1}}$ for **2**. After 22 h, TONs of 1100 and 1400 were obtained for **1** and **2**, respectively.

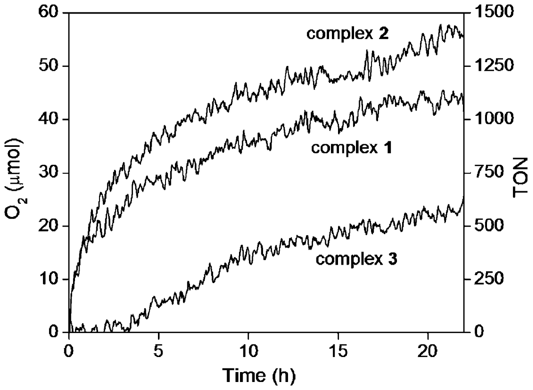


Figure 6. Kinetics of oxygen evolution induced by Ce^{IV} (330 mM) in aqueous CF_3SO_3H (pH 1.0, 3 mL) in the presence of catalyst (13.3 μM). The curves were measured with an O_2-sensor and calibrated by GC.

The TONs of **1** and **2** are more than twice as high as those of Thummel's dimeric complexes (TONs < 700),[13] showing that they are indeed more efficient catalysts than the complexes **C**. There could be two reasons for this catalytic efficiency difference. Firstly, the uncomplexed nitrogen in the naphthyridine moieties of Thummel's complexes **C** (see Scheme 1) was intended to provide hydrogen bonding with water.[12] Under pH 1 conditions, however, this uncomplexed nitrogen is probably protonated and so would become an electron-withdrawing group, which would decrease the catalytic activities of the complexes **C** in a similar way as the electron-withdrawing group (CF_3) at the axial position of pyridines, as observed by Thummel and co-workers.[12] Secondly, the electron-donating alkyl groups in the ligands **L1** and **L2** can facilitate oxidation processes and thus enhance the catalytic performance of complexes **1** and **2**.

On the other hand, the TONs and TOFs of **1** and **2** are only 10 to 40% of those of the complex **E**,[22] showing that the complexes **1** and **2** are much less stable and less active than the complex **E**. The improvement in the catalytic activity of the metal complexes achieved by introduction of alkyl groups is therefore far less than that achieved by use of negatively charged ligands. This is because the anionic ligands are more efficient electron-donating groups, capable of reducing the charge accumulation on the metal complexes generally and of lowering the oxidation potentials of the metal ions, and thus of stabilising the high oxidation states of the metal ions and providing a low-energy pathway for oxidising water.

When the complex **3** was used as catalyst, unlike **1** and **2**, it needed a long induction period (ca. 3 h) to produce detectable amount of oxygen (see also Figure 6). After a reaction time of 22 h, a TON of 568 was obtained for **3**. This result indicates that the complex **3** is not a true water oxidation catalyst and that ligand exchange between the 4-methylpyridyl ligand and free water molecules occurs to form the real water oxidation catalyst. This phenomenon has also been observed in the case of $[Ru(tpy)(pic)_3]^{2+}$ (tpy = terpyridine; pic = 4-methylpyridine), which has a structural similarity to **3**.[14] Most probably, complex **3** and $[Ru(tpy)(pic)_3]^{2+}$ have similar reaction mechanisms.

Previously, the true catalyst corresponding to $[Ru(tpy)(pic)_3]^{2+}$ (*trans*-$[Ru(tpy)(pic)_2(OH_2)]^{2+}$) was successfully prepared and proved active for water oxidation; oxygen evolution is first order in *trans*-$[Ru(tpy)(pic)_2(OH_2)]^{2+}$, implying that a mononuclear catalytic pathway is involved.[14] In the light of our findings and of fruitful mechanistic studies on $[Ru(tpy)(bpy)(OH_2)]^{2+}$ (bpy = bipyridine),[8,36] we propose that **3** needs ligand exchange between coordinated pic and free water to generate the Ru-aqua complex, which in turn catalyses water oxidation in the manner of water nucleophilic attack on the Ru=O species.

In our previous work we have demonstrated that low concentrations of Ce^{IV} benefit the catalytic activities of the two complexes **D** and **E**, very probably because the ligand decomposition is significantly reduced in the presence of a low concentration of Ce^{IV}.[22] Here, we also conducted the catalytic reaction in the presence of a relatively low concentration of Ce^{IV} (5 mM). As expected, the TONs for all three complexes were increased dramatically: TONs of 3500, 4500 and 2000 were achieved for **1**, **2** and **3**, respectively (Figure 7). These data imply that the performances of our catalysts might be further improved under milder catalytic conditions, such as in an electrolyser. Immobilisation of these catalysts might therefore be an attractive way to produce active water oxidation electrodes based on molecular catalysts.

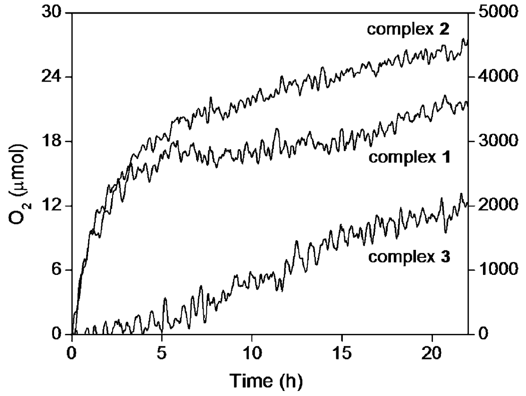


Figure 7. Kinetics of oxygen evolution induced by Ce^{IV} (5 mM) in aqueous CF_3SO_3H (pH 1.0, 30 mL) in the presence of the catalyst (0.2 μM). The curves were measured with an O_2-sensor and calibrated by GC.

^{18}O-Isotopic labelling studies: An essential question in water oxidation is whether or not the oxygen atoms in the evolved O_2 originate from the water. The use of ^{18}O-labelled water together with mass spectroscopy enabled us to determine the source of the O atoms in the evolved O_2, by evaluation of the ratio between the oxygen isotopes in the evolved O_2. Figure 8 shows the traces of evolved O_2 with m/z 32 ($^{16/16}O_2$) and 34 ($^{16/18}O_2$) on addition of a solution of **1** (0.15 mL) in acetonitrile to an aqueous solution containing isotope-enriched H_2O (10% ^{18}O, 0.3 mL), CF_3SO_3H (5 μL) and Ce^{IV} (100 mg). (The trace for $^{18/18}O_2$ could not be determined exactly, due to the presence of ^{36}Ar.) The observed ratio of evolved O_2 with masses 34 and 32 was found to be 0.23, which is very close to the theoretical ratio (2:9 = 0.22) based on the assumption that both O atoms of O_2 come from H_2O containing 10% $^{18}OH_2$. This ratio did not change with time, so oxygen exchange between the oxidant and water can be ruled out. The conclusion that can be drawn from this result is that water is the only source of the evolved oxygen in water oxidation catalysed by **1**.

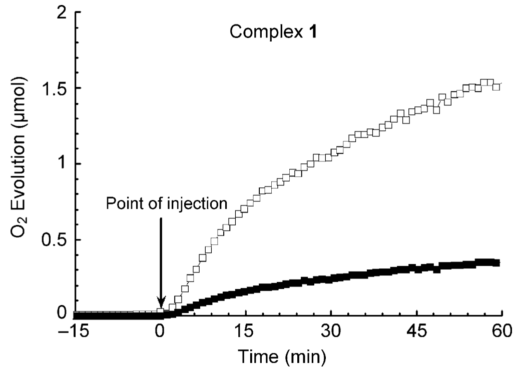


Figure 8. $^{16/16}O_2$ (□) and $^{16/18}O_2$ (■) evolution recorded by mass spectroscopy. An Ar-degassed solution of **1** in acetonitrile (0.15 mL) was injected into a mixture of Ce^{IV} (100 mg), CF_3SO_3H (5 μL) and ^{18}O-enriched H_2O (0.3 mL, 10% ^{18}O) (under Ar, ≈75 mbar).

ESI-MS analysis: ESI-MS has been used to probe reaction intermediates under catalytic conditions.[36b] We conducted ESI-MS measurements to isolate any intermediate related to the **2**·Ce^{IV} catalytic system in situ. Figure 9 and Figure S1 in the Supporting Information show the mass spectra of identified species after addition of Ce^{IV} (200 equiv) to aqueous complex **2**. We observed the singly charged species $[M{-}3PF_6{+}2CF_3SO_3]^+$ at 1337.10 (calcd: 1337.09), $[M{-}3PF_6{+}O{+}2CF_3SO_3]^+$ at 1353.13 (calcd: 1353.08) and $[M{-}3PF_6{+}2O{+}2CF_3SO_3]^+$ at 1369.05 (calcd: 1369.08), as well as the doubly charged species $[M{-}3PF_6{-}pic{+}CF_3SO_3]^{2+}$ at 547.59 (calculated: 547.54) and $[M{-}3PF_6{-}2pic{+}CF_3SO_3]^{2+}$ at 501.05 (calculated: 501.01), where M refers to the formula of complex **2**. We note that a few MS peaks are unidentifiable. After addition of ascorbic acid (80 equiv) to the above solution, the MS peaks for $[M{-}3PF_6{+}O{+}2CF_3SO_3]^+$ and $[M{-}3PF_6{+}2O{+}2CF_3SO_3]^+$ still remain, revealing that these two species are ligand-oxidised products rather than seven-coordinate Ru oxo species.

From these observations, we propose ligand-exchange species such as Ru_2OH_2 and $Ru_2(OH_2)_2$ (Scheme 5) as the true water oxidation catalysts for the **2**·Ce^{IV} catalytic system. The aquo ligand could lower the oxidation potentials of the metal centre through proton-coupled electron transfer (PCET), potentially allowing Ce^{IV} to drive Ru_2OH_2 and $Ru_2(OH_2)_2$ to oxidise water. At this stage, however, we could not exclude the possibility that water coordinates to

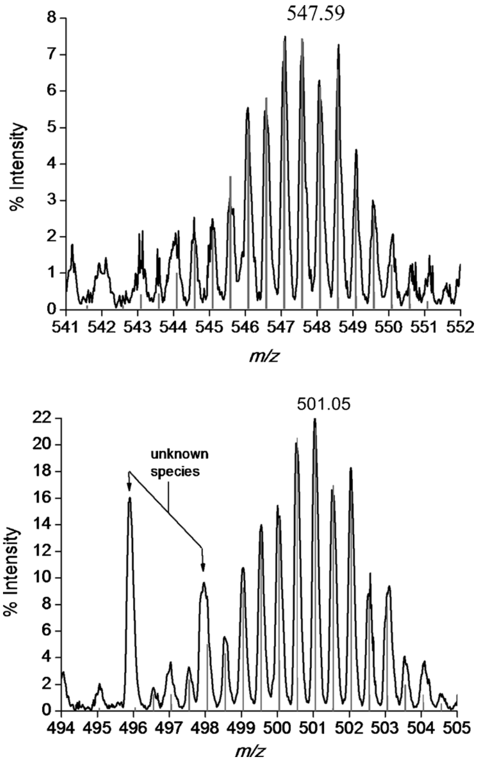
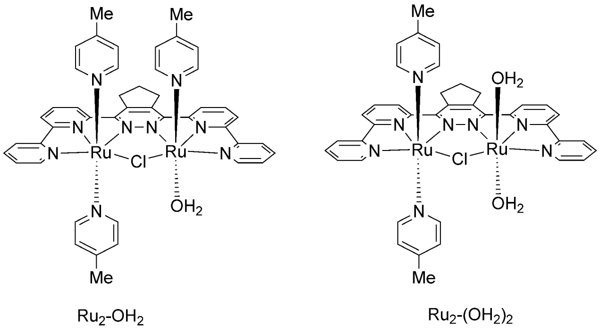


Figure 9. Observed (curves) and simulated (bars) isotope pattern. Upper: $[M{-}3PF_6{-}pic{+}CF_3SO_3]^{2+}$ observed: 547.59; calculated: 547.54. Lower: $[M{-}3PF_6{-}2pic{+}CF_3SO_3]^{2+}$ observed: 501.05; calculated: 501.01.



Scheme 5. Structures of Ru_2OH_2 and $Ru_2(OH_2)_2$ (isomers not shown).

the ruthenium metal as a seventh ligand without loss of picolines.

Conclusion

The three Ru-based precatalysts **1**–**3** for Ce^{IV}-driven water oxidation have been synthesised and characterised. Under optimised catalytic conditions, large TONs of 3500, 4500 and 2000 have been achieved with complexes **1**, **2** and **3**, respectively. Isotope labelling studies are consistent with the atoms in the evolved oxygen originating only from water. Detailed electrochemical and ESI-MS studies suggest that ligand exchange is necessary for **1**–**3** to form the true real water oxidation catalysts. Ligand modification demonstrated that the catalytic activities could be promoted by introducing electron-donating functional groups on the neutral ligands. Although these complexes exhibit relatively high turnover numbers, they are much less efficient catalysts for water oxidation than the complexes with negatively charged ligands. These results, together with our previous investigations, could provide useful insights in the design of efficient water oxidation catalysts by ligand modification.

Experimental Section

Materials: All chemicals were purchased from Sigma–Aldrich or Lancaster and used as received. All solvents were dried by standard methods when needed. Compound **9** was prepared by the literature method.[38]

NMR spectroscopy: 1D and 2D NMR spectra were recorded with a Bruker Avance 400/500 MHz spectrometer.

Mass spectrometry: Mass spectrometry measurements were performed either with a Q-Tof Micro mass spectrometer (HRMS, Micromass, Manchester, UK) or with a LCQ ADVANTAGE MAX (Finnigan) mass spectrometer. The **2**·Ce^{IV} catalytic system was analysed by Q-Tof Micro mass spectrometry: typically a Ce^{IV} solution (20 mM in triflic acid, pH 1.0) was added to complex **2** (2 mM) in acetonitrile (0.2 mL) with vigorous stirring, during which the solution of **2** changed from deep purple to light brown; after about 10 min, the resulting solution was injected into the mass spectrometer.

UV/Vis absorption spectroscopy: The UV/Vis absorption spectrum was measured with a CARY 300 Bio UV/Vis spectrophotometer.

Electrochemistry: Cyclic voltammetry and differential pulse voltammetry were performed in acetonitrile and water, with an Autolab potentiostat and GPES electrochemical interface (Eco Chemie), a glassy carbon disk (diameter 3 mm, freshly polished) as the working electrode and a platinum wire in a compartment separated from the bulk solution by a fritted disk as counter-electrode. The electrolyte used was Bu_4NPF_6 in acetonitrile (0.1 M) or a mixture of aqueous CF_3SO_3H (pH 1) and acetonitrile (2:1, v/v). The reference electrode was Ag/Ag^+ in $AgNO_3$ in acetonitrile (0.01 M) or Ag/AgCl in aqueous KCl (3 M). Potentials versus NHE are calculated by adding +0.630 V to the potentials versus the Fc^+/Fc couple in acetonitrile and by use of the $Ru^{3+/2+}$ redox couple of $Ru(bpy)_3Cl_2$ as standard with $E_{1/2} = 1.26$ V versus NHE in aqueous solution. Half-wave potentials ($E_{1/2}$) were determined by cyclic voltammetry as the averages of the anodic and cathodic peak potentials $[E_{1/2} = (E_{pa}+E_{pc})/2]$. Reversibility was determined from the peak-to-peak separations ΔE_p ($\Delta E_p = E_{pa}-E_{pc}$) and the ratio of the anodic to cathodic peak currents (i_{pa}/i_{pc}). The glassware used was oven-dried, assembled and flushed with argon while hot. Before all measurements, solvent-saturated argon was bubbled through the stirred solutions and the samples were kept under argon during measurements.

Oxygen evolution analysis: The oxygen produced in the gas phase was measured with a 3000 A Micro GC (Agilent Technologies) fitted with a thermal conductive detector and a 5 Å molecular sieve column (12 μm/320 μm/10 m) allowing auto sampling and analysis at 66 °C. Helium was used as carrier gas. Data were calibrated with a standard gas mixture and air as the standard. In a typical run, a reaction flask containing a solution of Ce^{IV} in aqueous CF_3SO_3H solution (pH 1.0) was connected to the GC sampling system through a septum. The reaction mixture was stirred and deaerated with helium for 20 min. The oxygen content in the headspace of the flask was measured by GC, after which the catalyst in acetonitrile solution was injected into the flask through the septum by syringe. After 24 h, the O_2 content was measured again by GC. The amount of oxygen evolved was analysed. No leakage from air in the reaction flask was found by monitoring the N_2 content by GC.

The kinetics were followed simultaneously with the aid of an Ocean Optics oxygen sensor (FOXY-OR125-G) with a multifrequency phase fluorimeter (MFPF-100) connected to a PC. The sensor probe was inserted into the reaction flask described above through a septum. The oxygen content versus the reaction time was recorded with the oxygen sensor and calibrated with the data obtained from GC.

^{18}O-Labelling isotope ratio mass spectrometry: Mass spectrometry was employed to perform simultaneous measurement of the concentrations of various isotopomers of oxygen produced by the reaction mixture containing ^{18}O-labelled water, as described previously.[20] $Ce(NH_4)_2(NO_3)_6$ (100 mg, 0.18 mmol), ^{18}O-labelled water (10% ^{18}O) (0.3 mL) and CF_3SO_3H (5 μL) were mixed in the reaction vessel. Air in the reaction system was removed with a rough pump, prior to filling with argon to keep the pressure at ≈100 mbar. After 15–20 min, an Ar-degassed solution of the catalyst in acetonitrile (0.15 mL) was injected into the reaction vessel. The generated gases were measured and recorded against time.

4,4′-Dimethyl-2,2′-bipyridine *N*-oxide (5): The mono *N*-oxide **5** was prepared by the procedure used for the similar compound in ref. [38]. A suspension of 3-chloroperbenzoic acid (*m*-CPBA, 13.8 g, 50–60%, 40–48 mmol) in CH_2Cl_2 (100 mL) was added dropwise over 50 min at 5–10 °C to a solution of 4,4′-dimethyl-2,2′-bipyridine (**4**, 8.0 g, 43.4 mmol) in CH_2Cl_2 (100 mL). The mixture was stirred at room temperature overnight. Aqueous Na_2CO_3 (10%, 100 mL) was added at 0 °C and the mixture was stirred for 30 min. The organic phase was separated, washed once more with aqueous Na_2CO_3 (10%, 100 mL) and dried over solid Na_2CO_3. The solvent was removed and the crude product was purified by column chromatography on SiO_2 with MeOH in CH_2Cl_2 (5%) as eluent to afford the pure product (5.7 g, 66% yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.42 (s, 3H), 2.46 (s, 3H), 7.09 (dd, J=6.6, 2.6 Hz, 1H), 7.19 (dd, J=5.0, 0.6 Hz, 1H), 7.96 (d, J=2.4 Hz, 1H), 8.22 (d, J=6.6 Hz, 1H), 8.59 (d, J=5.0 Hz, 1H), 8.75 ppm (d, J=0.6 Hz, 1H).

6-Cyano-4,4′-dimethyl-2,2′-bipyridine (6): Compound **6** was prepared by the procedure used for the similar compound in ref. [38]. Me_3SiCN (**CAUTION!** Highly toxic cyanide equivalent: handle with care! 4.6 mL, 3.39 g, 34 mmol) was added at room temperature to a solution of **5** in CH_2Cl_2 (50 mL). After 5 min, dimethylcarbamoyl chloride (3.15 mL, 34 mmol) was added. The mixture was stirred at room temperature for 6 days. Aqueous $NaHCO_3$ (10%, 50 mL) was added and the mixture was stirred for 20 min. The organic phase was separated, washed once more with aqueous $NaHCO_3$ (10%, 50 mL) and then with brine, and dried over solid Na_2CO_3. The solvent was removed and the crude product was purified by recrystallisation from a mixture of diethyl ether and hexane to afford the pure product (4.69 g, 70% yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.49 (s, 3H), 2.52 (s, 3H), 7.22 (d, J=5.0 Hz, 1H), 7.55 (s, 1H), 8.32 (s, 1H), 8.50 (s, 1H), 8.56 ppm (d, J=5.0 Hz, 1H).

3,6-Bis-(4′,4″-dimethyl-2′,2″-bipyrid-6′-yl)-1,2-dihydro-1,2,4,5-tetrazine (7): This compound was prepared by the similar procedure in ref. [39]. Hydrazine hydrate (4.0 g, 98%, 78.3 mmol) was added to a suspension of **6** (4.16 g, 19.92 mmol) in ethanol (70 mL). The mixture became a clear brown solution on heating. It was gently heated at reflux for 24 h. The resulting yellow precipitate was filtered and washed with ethanol. The crude product was recrystallised from ethanol to give the dihydro base (1.67 g, 37%). ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.39 (s, 6H), 2.40 (s, 6H), 7.08 (dd, J=5.0, 0.8 Hz, 2H), 7.82 (s, 2H), 8.21 (s, 2H), 8.25 (s, 2H), 8.46 (d, J=5.0 Hz, 2H), 8.68 ppm (s, 2H).

3,6-Bis-(4′,4″-dimethyl-2′,2″-bipyrid-6′-yl)-1,2,4,5-tetrazine (8): This compound was prepared by a procedure similar to that in the literature.[39] Concentrated nitric acid (8 mL, 65%) was added dropwise to a suspension of **7** (1.67 g, 3.72 mmol) in acetic acid (60 mL) cooled with an ice-water bath. The mixture immediately turned red. After 30 min, excess ice was added and the mixture was neutralised by the addition of sodium bicarbonate. The precipitate was filtered and washed with ethanol to give the tetrazine **8** as a red solid (0.975 g, 59% yield). No NMR or MS data are available, due to the poor solubility of the product. The crude product was used in the next reaction without purification.

Ligand L1: This compound was prepared by a procedure similar to that in ref. [39]. Acetylene was slowly bubbled through a solution of **8** (0.97 g, 2.17 mmol) in DMF (25 mL) at reflux. After the red colour of the reaction mixture had disappeared, it was cooled down to room temperature. DMF was removed, and the crude product was purified by column chromatography on silica gel with acetone in CH_2Cl_2 (4%) as eluent to give the desired product (0.8 g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.53 (s, 6H), 2.59 (s, 6H), 7.20 (d, J=4.5 Hz, 2H), 8.39 (s, 2H), 8.43 (s, 2H), 8.60 (d, J=4.9 Hz, 2H), 8.67 (s, 2H), 8.92 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.80, 21.86, 122.43, 122.88, 123.37, 125.29, 125.62, 148.43, 149.41, 149.86, 153.00, 156.10, 156.23, 158.72 ppm.

3,6-Bis-(2′,2″-bipyrid-6′-yl)-1,2-dihydro-1,2,4,5-tetrazine (10): This compound was prepared by a procedure similar to that used for compound **7**. Treatment of compound **9** (9.36 g, 19.7 mmol) with hydrazine hydrate (4.5 mL, 55%, 79.6 mmol) in ethanol afforded compound **10** (2.0 g, 52% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.34–7.37 (m, 2H), 7.87 (td, J=8.0, 2.0 Hz, 2H), 7.93 (t, J=8.0 Hz, 2H), 8.09 (d, J=8.0 Hz, 2H), 8.49 (d, J=7.5 Hz, 2H), 8.52 (d, J=8.0 Hz, 2H), 8.70 (d, J=5.0 Hz, 2H), 8.73 ppm (s, 2H).

3,6-Bis-(2′,2″-bipyrid-6′-yl)-1,2,4,5-tetrazine (11): This compound was prepared by a procedure similar to that used for compound **8**. Oxidation of compound **10** (3.576 g, 23.88 mmol) with concentrated HNO_3 (10 mL, 65%) in acetic acid (100 mL) at 0 °C gave compound **11** (8.5 g, 91% yield).

Ligand L2: This ligand was prepared by a method similar to that reported by Schubert and co-workers.[40] A mixture of compound **11** (330 mg, 0.846 mmol), cyclopentanone (143 mg, 1.7 mmol), morpholine (140 mg, 1.6 mmol) and silica gel (210 mg) in toluene was heated at 110 °C for 5 h. After the mixture had been allowed to cool to RT, a white precipitate had formed. The mixture was filtered through celite and washed thoroughly with MeOH in CH_2Cl_2 (10%). The slightly yellow filtrate was collected and solvent was removed under reduced pressure. The desired product was obtained in 100% yield as a white powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.30 (quint., J=7.8 Hz, 2H), 3.76 (t, J=7.7 Hz, 4H), 7.34–7.37 (m, 2H), 7.89 (td, J=7.6, 1.6 Hz, 2H), 8.05 (t, J=7.8 Hz, 2H), 8.51 (d, J=7.9 Hz, 2H), 8.54 (d, J=7.7 Hz, 2H), 8.73 ppm (d, J=6.9 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=24.5, 34.1, 121.1, 123.5, 123.8, 137.0, 137.9, 145.5, 149.3, 155.1, 155.3, 155.4, 156.3 ppm.

Complex 1: A mixture of the ligand **L1** (100 mg, 0.226 mmol) and *cis*-$[Ru(dmso)_4Cl_2]$ (240 mg, 0.496 mmol) in ethanol (80 mL) was heated at reflux for one day. Water (10 mL), 4-methylpyridine (1.1 mL, 11.28 mmol), LiCl (50 mg, 1.19 mmol) and triethylamine (0.5 mL) were added, and the mixture was further heated at reflux for 2 days. Ethanol was removed and excess NH_4PF_6 was added. The precipitate was separated and purified by column chromatography on Al_2O_3 to give the desired product (120 mg, 36% yield). ^{1}H NMR (500 MHz, [D$_6$]acetone): δ=2.09 (s, 12H), 2.58 (s, 6H), 2.76 (s, 6H), 6.70 (d, J=6 Hz, 8H), 7.72 (d, J=6 Hz, 8H), 7.95 (d, J=5.5 Hz, 2H), 8.27 (s, 2H), 8.42 (s, 2H), 8.94 (s, 2H), 9.23 (s, 2H), 9.42 ppm (d, J=5.5 Hz, 2H); ^{13}C NMR (125 MHz, [D$_6$]acetone): δ=20.60, 21.20, 21.73, 125.49, 125.56, 126.92, 127.60, 129.03, 131.45, 148.64, 150.70, 151.43, 152.72, 153.44, 157.73, 159.72, 160.34, 163.72 ppm; HRMS (ESI): m/z: calcd for $[M-3PF_6]^{3+}$: 351.7384; found: 351.7380.

Complex 2: The ligand **L2** (214 mg, 0.5 mmol) and *cis*-$[Ru(dmso)_4Cl_2]$ (484 mg, 1.0 mmol) were mixed in ethanol (30 mL). The mixture was heated at reflux overnight. Et_3N (1 mL), 4-picoline (1 mL) and LiCl (90 mg) were added, and the mixture was further heated at reflux for 24 h. Most of the solvent was removed, and the residue was washed with ether and purified by chromatography on silica gel, with use of a mixture of acetonitrile/H_2O/KNO_3 (sat.) (30:1:1) as eluent, and finally treated with NH_4PF_6, to afford the title complex (330 mg, 45% yield). ^{1}H NMR (500 MHz, CD_3CN): δ=2.03 (s, 12H), 2.79 (quint, J=7.8 Hz, 2H), 4.09 (t, J=7.9 Hz, 4H), 6.53 (d, J=6.2 Hz, 8H), 7.44 (d, J=6.4 Hz, 8H), 7.98–8.08 (m, 8H), 8.16 (d, J=8.0 Hz, 2H), 8.69 (d, J=8.4 Hz, 2H), 9.34 ppm (d, J=5.3 Hz, 2H); ^{13}C NMR (125 MHz, CD_3CN): δ=20.6, 24.7, 34.5, 124.1, 124.6, 126.7, 130.3, 130.9, 135.3, 140.3, 150.8, 151.0, 151.3, 152.9, 158.4, 160.0, 160.6, 161.4 ppm. ESI-MS: m/z: 346.16 (calcd for $[M-3PF_6]^{3+}$: 346.39), 592.06 (calcd for $[M-2PF_6]^{2+}$: 592.07), 1328.93 (calcd for $[M-PF_6]^{+}$: 1329.11).

$[Ru(L2)(dmso)Cl_2]$: A solution of *cis*-$[Ru(dmso)_4Cl_2]$ (96 mg, 0.198 mmol) and **L2** (42 mg, 0.098 mmol) in EtOH (4 mL) was heated at

70 °C for 0.5 h. A black precipitate was obtained by filtration, washed with EtOH and dried in vacuo (yield 82 mg, 96 %). ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 10.13$ (d, $J = 5.19$ Hz, 1 H), 8.74 (d, $J = 4.18$ Hz, 1 H), 8.61 (d, $J = 7.69$ Hz, 1 H), 8.40 (d, $J = 7.78$ Hz, 1 H), 8.23 (d, $J = 8.22$ Hz, 1 H), 8.19 (d, $J = 12.37$ Hz, 1 H), 8.17 (d, $J = 12.67$ Hz, 1 H), 8.10 (t, $J = 8.29$ Hz, 1 H), 7.95 (t, $J = 8.00$ Hz, 1 H), 7.89–7.81 (m, 2 H), 7.52 (t, $J = 6.40$ Hz, 1 H), 7.38 (t, $J = 6.50$ Hz, 1 H), 3.79 (s, 6 H), 3.73 (t, $J = 7.50$ Hz, 2 H), 3.56 (t, $J = 7.48$ Hz, 2 H), 2.38 ppm (quint, $J = 7.02$ Hz, 2 H); ESI-MS: m/z: 679.0 (calcd for $[M+H]^+$: 679.0) and 701.0 (calcd for $[M+Na]^+$: 701.0).

Complex 3: A mixture of [Ru(**L2**)(dmso)Cl$_2$] (44 mg, 0.064 mmol) and 4-picoline (0.5 mL) in EtOH/H$_2$O (10 mL, 9:1 v/v) was deoxygenated (N$_2$) and heated at reflux overnight. The solvent was evaporated and the residue was dissolved in H$_2$O (5 mL), to which excess NH$_4$PF$_6$ aqueous solution had been added. The formed precipitate was collected and washed with water. The crude product was purified by column chromatography on silica gel with acetonitrile/KNO$_3$/H$_2$O 40:1:1 as eluent. The red band was collected and solvents were removed. The resulting solid was dissolved in a small amount of CH$_3$CN/H$_2$O and then NH$_4$PF$_6$ was added. Evaporation of CH$_3$CN resulted in the formation of precipitate, which was washed with water and dried under vacuum to provide a red solid (37 mg, 52 %). ^{1}H NMR (400 MHz, MHz, CD$_3$CN): $\delta = 8.74$ (m, 2 H), 8.62 (d, $J = 7.93$ Hz, 1 H), 8.54–8.47 (m, 4 H), 8.38 (d, $J = 5.22$ Hz, 2 H), 8.36 (d, $J = 8.32$ Hz, 1 H), 8.20 (t, $J = 7.81$, 7.81 Hz, 1 H), 8.17–8.08 (m, 2 H), 7.98 (t, $J = 7.03$ Hz, 1 H), 7.84–7.78 (m, 1 H), 7.53–7.44 (m, 3 H), 7.34 (d, $J = 5.33$ Hz, 4 H), 6.82 (d, $J = 5.78$ Hz, 4 H), 3.91 (t, $J = 7.74$ Hz, 2 H), 3.65 (t, $J = 7.72$ Hz, 2 H), 2.60 (s, 3 H), 2.41 (quint, $J = 7.27$ Hz, 2 H), 2.15 ppm (s, 6 H); ESI-MS: m/z: 404.52 (calcd for $[M-2\,PF_6]^{2+}$: 404.63), 953.87 (calcd for $[M-PF_6]^+$: 954.22).

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