Structural properties of trans hydrido–hydroxo $M(H)(OH)(NH_2CMe_2CMe_2NH_2)(PPh_3)_2$ ($M = Ru, Os$) complexes and their proton exchange behaviour with water in solution

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Structural Properties of *Trans* Hydrido-Hydroxo $M(H)(OH)(NH_2CMe_2CMe_2NH_2)(PPh_3)_2$ ($M =$ Ru, Os) Complexes and their Proton Exchange Behaviour with Water in Solution

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Abstract

We report the synthesis of Ru(II) and Os(II) *trans* hydrido-hydroxo complexes by reacting the unsaturated amido complexes $MH(NHCMe_2CMe_2NH_2)(PPh_3)_2$ ($M = Ru, Os$) with stoichiometric amounts of water. Proton exchange is rapid at room temperature between the amine/water/hydroxide moieties which leads to signal averaging of the NMR properties which can be slowed at low temperature in order to see resonances of separate complexes. These compounds can also be cleanly converted back to their starting complexes by dehydration in the presence of 3 Å molecular sieves. X-ray crystal structures of these Ru(II) and Os(II) *trans* hydrido-hydroxo complexes reveal that the unit cell contains an additional molecule of water trapped in the crystal lattice which hydrogen bonds with a neighbouring hydroxo ligand, forming a water bridged dimer in the solid state. Although there are many cases of oxidative addition of water to transition metal complexes, relatively few cases are known where water addition occurs via metal-ligand cooperation (bifunctional addition) without altering the oxidation state of the metal center.

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1 Introduction

Water is a very attractive chemical feedstock to produce hydrogen as an energy resource due to its vast abundance on Earth. Therefore, the reactivity of transition metal complexes with water has important implications in developing well-defined catalysts that can convert H_2O into H_2 and/or O_2 .¹ In general, the intramolecular splitting of a water O-H bond at a well-defined metal complex can be facilitated in two ways: (a) water can be oxidatively added, therefore increasing the metal's oxidation state by two and creating new M-H and M-OH bonds;² (b) water can add in a cooperative metal-ligand fashion where the hydroxide ion binds to the metal center and the ligand system is protonated, leaving the metal's oxidation state unchanged. In the latter case, this can be achieved using monodentate oxo ligands on high oxidation state transition metal complexes,³ a bidentate amino-amido ligand,⁴ or a tridentate PNN-type pincer ligand.⁵ While there have been many reports of water adding to transition metal complexes via oxidative addition or using high-valent metal-oxo compounds, there are relatively few studies of intramolecular metal-ligand water addition using multidentate bifunctional ligands.^{4,5} Furthermore, NMR characterization can be challenging because the resultant complexes may rapidly exchange protons on the NMR time scale which broadens signals of interest.^{6,7}

In our efforts to understand how bifunctional metal-amido containing complexes react with water, we report the ^1H NMR, ^{31}P NMR, and structural characterization when the five-coordinate ruthenium(II) and osmium(II) metal-amido complexes of the general formula $\text{MH}(\text{NHCM}_2\text{CMe}_2\text{NH}_2)(\text{PPh}_3)_2$ ($\text{M} = \text{Ru, Os}$) are exposed to stoichiometric amounts of H_2O . These Ru and Os amido complexes have been previously studied by our group as catalysts for the hydrogenation of polar bonds⁸ and for Michael additions.^{8e} Both complexes reversibly cleave the O-H bond of H_2O across the metal-amido fragment to produce *trans*- $\text{MH}(\text{OH})(\text{NH}_2\text{CMe}_2\text{CMe}_2\text{NH}_2)(\text{PPh}_3)_2 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Ru, } n = 0, 1; \text{M} = \text{Os, } n = 1$) which are only clearly observable at low temperatures by ^1H NMR spectroscopy. The addition of stoichiometric equivalents of water changes the appearance of the ^1H NMR spectra and provides information on proton exchange

equilibria occurring in solution. Furthermore, we also report molecular structures of these products which contain an additional water molecule in the crystal lattice that acts as a hydrogen bonding bridge between neighbouring metal complexes.

2 Results and discussion

We mixed the highly reactive five-coordinate ruthenium hydrido-amido complex $\text{RuH}(\text{NHCMe}_2\text{CMe}_2\text{NH}_2)(\text{PPh}_3)_2$ (**1Ru**) with one equivalent of H_2O in an NMR tube in toluene- d_8 (Scheme 1). The ^1H NMR spectrum at 25 °C (aromatic region excluded) shows broad signals at 2.88 and 0.88 ppm and a triplet at -17.5 ppm (Scheme 1a, black line) with no detectable amount of **1Ru**. These three signals integrate to a 5:12:1 ratio, respectively, and we assign them as follows: the broad signal at 2.88 ppm is a combination of NH and OH protons; the signal at 0.88 ppm belongs the methyl groups on the diamine backbone; the triplet at -17.5 ppm is the metal hydride with a $^2J_{\text{HP}}$ coupling constant of 25 Hz, consistent with being *cis* to both PPh_3 ligands.

scheme 1: Reaction of **1Ru** with H_2O .

Cooling the sample to -60 °C significantly changes the appearance of the signals in Scheme 1a (green line). The signal originally at 2.88 ppm separates into two distinct peaks at 3.73 and 1.95 ppm (labelled NH_a and NH_b , respectively), each accounting for two protons. Based on the chemical shift of these four protons as compared to similar $\text{RuHX}(\text{NH}_2\text{CMe}_2\text{CMe}_2\text{NH}_2)(\text{PPh}_3)_2$ complexes,^{8c} we assign these to be the NH

protons belonging to the compound *trans*-Ru(H)(OH)(NH₂CMe₂CMe₂NH₂)(PPh₃)₂ (**2Ru**). The methyl resonance has resolved into two distinct signals at 0.89 and 0.74 ppm and the hydride signal has shifted upfield to -16.9 ppm. Observing two CH₃ signals at -60 °C is also consistent with the presence of unique chemical environments above and below the plane of the Ru-diamine metallacycle. At room temperature, there is signal averaging over all four methyl groups as a result of the rapid interconversion between their axial and equatorial positions,^{8e} whereas at low temperatures these methyl groups resolve into two discrete signals. A new signal appears at -1.51 ppm accounting for one more proton which we assign to be the Ru-OH moiety, correlating well with other known monomeric *trans*-Ru(H)(OH)L₄ complexes.^{4-6,9} A very broad and weak signal centered at -21.1 ppm is detectable at -60 °C which is characteristic of the starting complex **1Ru**. Therefore, we conclude that at room temperature there is rapid exchange between NH and OH protons while at low temperatures the observed compound is predominantly **2Ru**. The hydride signal position at room temperature (-17.5 ppm) can then be considered a weighted average of the fraction of **1Ru** and **2Ru** in solution whose signals can be separated at low temperatures. Taking the chemical shift of the product complex (-16.9 ppm) and the starting material (-21.1 ppm) with their weighted average found at -17.5 ppm at room temperature means that there is about 14% **1Ru** and 86% **2Ru** at 25 °C. Moreover, an intermediate amido-aqua complex is not observed at temperatures between 25 °C and -80 °C. If 3 Å molecular sieves are added to the reaction mixture at room temperature, the exclusive product is the starting material **1Ru**, demonstrating the labile nature of the water molecule. Reacting **1Ru** with one equivalent of D₂O followed by probing the reaction solution at -60 °C via ¹H NMR resulted in a decrease of signal intensity for peaks NH_a, NH_b and the Ru-OH, leaving the hydride, methyl, and phenyl protons unchanged. This supports the notion that rapid proton exchange is localized to the nitrogen and oxygen atoms.

If two equivalents of water are added to an NMR tube filled with **1Ru** in toluene-*d*₈, the orange reaction solution turns yellow after a few seconds of shaking and variable temperature ¹H NMR experiments were performed (Scheme 1b). At room temperature (black line), we rationalize that the broad five-proton signal at 2.74 ppm is the signal

Figure 1: (a) Overlaid ^1H NMR spectra (400 MHz) of $1\text{Ru} + \text{H}_2\text{O}$ at 25°C (black) and -60°C (green). (b) Overlaid ^1H NMR spectra (400 MHz) of $1\text{Ru} + 2\text{H}_2\text{O}$ at 25°C (black), -40°C (green), and -80°C (blue). Residual solvent signal (CD_3) for toluene- d_8 appears at 2.09 ppm. Only the inset spectrum on the bottom left was obtained using a 600 MHz NMR spectrometer to increase the resolution of the H_2O signal. The aromatic resonances appear from 8.0–6.8 ppm and some have been omitted and some spectra have been magnified on the y-axis for clarity.

averaging of three groups of protons: two diamine protons NH_a , H_2O , and a Ru-OH proton. The remaining two diamine protons, NH_b , can be clearly seen at 1.94 ppm at 25 °C. Resolution in the methyl region (0.95 and 0.74 ppm) at room temperature indicates unique chemical environments above and below the diamine metallacycle. The Ru-H signal appears upfield at -17.41 ppm as a triplet, maintaining its 25 Hz coupling constant due to neighbouring *cis* phosphines.

When the temperature is decreased to -40 °C, the broad five-proton signal at 2.74 ppm disappears and a new signal appears at 3.75 ppm belonging to NH_a (Scheme 1b, green line). The two-proton signal formerly at 1.94 ppm shifts slightly to 1.89 ppm. However, there are three protons, belonging to the ruthenium hydroxide and water moieties, which are not visible at -40 °C. Cooling the NMR sample down to -80 °C (Scheme 1b, blue line) reveals a broad signal at -1.24 ppm belonging to the Ru-OH moiety. In addition, a very broad signal becomes visible at 6.48 ppm (inset, Scheme 1b), which partly overlaps with the phenyl protons of PPh_3 . We assign this to be the second water molecule which reveals the presence of *trans*-Ru(H)(OH)($\text{NH}_2\text{CMe}_2\text{CMe}_2\text{NH}_2$)(PPh_3)₂· H_2O (**3Ru**) in solution. The severe broadening of the H_2O and OH peaks when they become visible at -80 °C suggests that proton exchange between these two moieties is much more rapid than the NH-OH proton exchange. As with **2Ru**, **3Ru** can be dehydrated to produce **1Ru** in quantitative yield in the presence of 3 Å molecular sieves. Signals belonging to **1Ru** could not be detected at any temperature between 25 °C and -80 °C, suggesting that the equilibrium lies much further toward the product side.

The diamine protons NH_b which appear at about 1.8 ppm at low temperatures in Scheme 1 are syn-coplanar to the metal hydride (Scheme 2). As the diamine conformation changes in solution, H_b is either in an axial position (syn-coplanar to the hydride) or equatorial which renders it unavailable to H-bond with water. H_a , on the other hand, is either equatorial or anti-coplanar to the hydride, which makes it available to form a six-membered ring with the water and hydroxide moieties; as a result, these protons become de-shielded and appear at about 3.8 ppm. This behaviour was also observed in a previous study where **1Ru** was reacted with weak acids HX, where X contains an oxygen atom available to participate in hydrogen bonding.^{8e} Furthermore, the same

study showed that the reaction of **1Ru** with two equivalents of phenol crystallizes to form $\text{RuH}(\text{OPh})(\text{NH}_2\text{CMe}_2\text{CMe}_2\text{NH}_2)(\text{PPh}_3)_2 \cdot \text{HOPh}$, in which the OH group on phenol forms a six-membered H-bonding ring by situating itself between a coordinated phenoxide oxygen and an amine proton. Our attempts to spectroscopically detect the selective proton exchange behaviour in the reaction of **1Ru** + 2 H_2O using low temperature ^1H – ^1H EXSY experiments were unsuccessful due to the overly broad amine and hydroxide resonances.

scheme 2: Hydrogen bonding equilibria in solution when reacting **1Ru** with two equivalents of H_2O .

In a related reaction, Bergman and co-workers reacted $\text{Ru}(\text{DMPE})_2(\text{C}_2\text{H}_4)$ (DMPE = dimethylphosphinoethane) with excess H_2O at 90 °C followed by crystallization to obtain [*trans*- $\text{RuH}(\text{OH})(\text{DMPE})_2(\mu\text{-H}_2\text{O})$]₂ (**4**) which is a water bridged dimer in the solid state.⁶ Variable temperature NMR experiments were also performed on complex **4**, and at room temperature, a broad signal was detected at 2.30 ppm in $\text{THF-}d_8$, as compared to 2.9 ppm for **3Ru** in $\text{toluene-}d_8$. Upon cooling **4** to -92 °C, the water protons were assigned as a broad signal at 5.70 ppm and the broad hydroxide proton appeared at -4.55 ppm, as compared to 6.48 and -1.24 ppm for **3Ru**, respectively. The similarities between our findings and those of Bergman and co-workers further support our peak assignments. Furthermore, Piers and co-workers recently observed rapid and temperature dependant proton exchange between *cis* aqua-hydroxo ligands on a sterically bulky $\text{Pd}(\text{OH})(\text{H}_2\text{O})(\alpha\text{-diimine})$ complex.⁷

Given the temperature dependant spectral data of **4**, Bergman and co-workers were unable to determine its structure in solution, presumably uncertain whether the compound was monomeric or dimeric since the molecular structure afforded a water-bridged

dimer. We tried to determine whether our complex **3Ru** was monomeric or dimeric in solution by running Diffusion Ordered Spectroscopy (DOSY) NMR experiments at room temperature and comparing the self-diffusion constants of the amido complex **1Ru** and **3Ru**. We determined that the self-diffusion constant of **1Ru** is $5.5 \times 10^{-10} \pm 0.5 \text{ m}^2/\text{s}$ and $5.3 \times 10^{-10} \pm 0.2 \text{ m}^2/\text{s}$ for **3Ru**, indicating that the overall difference in size of the individual molecules in solution is indistinguishably small, and therefore **3Ru** remains monomeric in solution. Due to the temperature dependant spectral similarities and similar crystal packing of **3Ru** and **4** (vide infra), we expect that **4** is also monomeric in solution.

Given the recent successes in consecutive thermal and photochemical evolution of H_2 and O_2 by a Ru-PNN pincer complex,⁵ we were interested to determine whether **3Ru** could evolve H_2 by releasing a proton from the diamine ligand and hydride from the metal center, followed by addition of the second equivalent of H_2O across the metal-amido bond to generate a bis(hydroxo) complex. NMR scale reactions in toluene- d_8 were carried out after injection of two equivalents of H_2O to **1Ru** where either (a) the sample was heated up to 90°C or (b) the sample was irradiated with ultraviolet light at room temperature. Both reaction solutions gradually changed from yellow to dark orange and were monitored by ^{31}P and ^1H NMR. In both the thermolysis and photolysis reactions, decomposition occurred by dissociation of the phosphine and diamine ligands which was accompanied by the formation of triphenylphosphine oxide ($\text{PPh}_3=\text{O}$). After several days, the only detectable phosphorus-containing product in the photolysis reaction was $\text{PPh}_3=\text{O}$. Oxidation of the phosphine by water might be accompanied by reduction to $\text{Ru}(0)$, which has been demonstrated for the case of palladium-catalyzed aryl halide activation.¹⁰ Furthermore, no detectable amounts of free H_2 were identified in the ^1H NMR spectra. Attempts to synthesize a bis(hydroxo) complex by using N_2O to transform the metal hydride into a metal hydroxide moiety⁹ led to the immediate formation of $\text{PPh}_3=\text{O}$ and subsequent decomposition of the metal complex.

The difference in metal-amido bond strength between the analogous ruthenium and osmium complexes is apparent when **1Os** is reacted with one or two equivalents of H_2O . With only one equivalent of H_2O present, the complex

Table 1: Chemical shifts of interest (ppm) in the ^1H NMR spectra (400 MHz, toluene- d_8) of **1Ru** + 2 H_2O at $-80\text{ }^\circ\text{C}$ and **1Os** + 2 H_2O at $-60\text{ }^\circ\text{C}$.

Peak Assignment	Chemical Shift (ppm)	
	1Ru + 2 H_2O	1Os + 2 H_2O
H_2O	6.48	6.10
NH_a	3.88	4.06
NH_b	1.86	2.45
M–OH	-1.17	-0.71
M–H	-17.63	-19.01

trans-Os(H)(OH)($\text{NH}_2\text{CMe}_2\text{CMe}_2\text{NH}_2$)(PPh_3) $_2$ is not observed at low temperatures; instead, there is a 1:1 ratio of **1Os** and *trans*-Os(H)(OH)($\text{NH}_2\text{CMe}_2\text{CMe}_2\text{NH}_2$)(PPh_3) $_2 \cdot \text{H}_2\text{O}$ (**3Os**) in solution (Scheme 3). This equilibrium is rationalized by the fact that 5d metals tend to prefer metal-ligand multiple bonds over 4d metals,¹¹ especially in the case of **1Ru** versus **1Os**.^{8d} When a second equivalent of water is added, **1Os** is present in lower quantities and the major product at low temperatures is **3Os**. Based on the relative integrations of the hydride and NH regions of **1Os** and **3Os** at $-60\text{ }^\circ\text{C}$, we estimate that there is about 25% **1Os** and 75% **3Os** in solution. The spectral features of **3Os** are similar to those of **3Ru** and a summary of key peak assignments is reported in Table 1. ^1H NMR spectra for these reactions are provided in the Supporting Information.

scheme 3: Reactions of **1Os** with H_2O .

We were able to obtain molecular structures of **3Ru** and **3Os** by growing crystals from a concentrated solution of each respective metal-amido complex and 2 equivalents of H_2O . Both ruthenium and osmium compounds share strikingly similar metrical parameters (Table 2) and only the structure of **3Ru** will be discussed. Complex **3Ru**

Figure 2: Left: Asymmetric unit of **3Ru** depicted with thermal ellipsoids at the 30% probability level. Hydrogen atoms on aromatic rings and methyl groups have been omitted for clarity. Selected bond distances and angles are listed in Table 2. Right: Crystal packing of **3Ru** as a water bridged dimer depicted with thermal ellipsoids at the 30% probability level. Phenyl carbons/hydrogens and methyl hydrogens have been omitted for clarity.

conforms to an octahedral geometry with an acute diamine bite angle (N1–Ru1–N2) of 74.4(1) degrees and an obtuse P1–Ru1–P2 angle of 96.68(3) degrees (Figure 2, left). The oxygen atom bonded to ruthenium is angled towards the diamine ligand (N1–Ru–O1 and N2–Ru–O1 angles of 80.77(9) and 80.9(1) degrees, respectively), with the distance between the closest two NH hydrogens and oxygen atom being less than the sum of their Van der Waals radii ($O1 \cdots H1A = 2.504 \text{ \AA}$ and $O1 \cdots H2B = 2.649 \text{ \AA}$, respectively). The oxygen of the hydroxo ligand acts as an H-bond acceptor while a neighbouring water molecule is the H-bond donor ($O1 \cdots O2 = 2.692(4) \text{ \AA}$). Pertinent crystal structure and refinement data are summarized in Table 3.

The crystal packing of **3Ru** reveals a hydrogen bonded dimer in which two water molecules act as H-bond donors for two hydroxo ligands (Figure 2, right). The second molecule of **3Ru** is related to the first by an inversion centre located in the middle of the $O \cdots O \cdots O \cdots O$ ring. The protons belonging to the hydroxo ligands do not participate in hydrogen bonding and are positioned between two phenyl rings. This unusual type of crystal packing motif has been reported by Bergman and co-workers (**4**, as mentioned above).⁶

To our knowledge, the only structurally characterized monomeric Ru(H)(OH) com-

Table 2: Selected Bond Lengths (Å) and Bond Angles (°) for **3Ru** and **3Os**.

3Ru		3Os	
Ru1–N1	2.182(3)	Os1–N1	2.185(4)
Ru1–N2	2.185(3)	Os1–N2	2.186(5)
Ru1–P1	2.2485(9)	Os1–P1	2.241(1)
Ru1–P2	2.2506(8)	Os1–P2	2.250(1)
Ru1–H1Ru	1.61(3)	Os1–H1Os	1.57(5)
Ru1–O1	2.190(2)	Os1–O1	2.192(3)
O1...O2	2.692(4)	O1...O2	2.709(6)
N1–Ru1–N2	74.4(1)	N1–Os1–N2	74.5(2)
P1–Ru1–P2	96.68(3)	P1–Os1–P2	98.82(5)
N1–Ru1–O1	80.77(9)	N1–Os1–O1	79.6(1)
N2–Ru1–O1	80.9(1)	N2–Os1–O1	80.2(1)
O1–Ru1–H1Ru	170(1)	O1–Os1–H1Os	163(2)

plexes are those of Bergman and co-workers (**4**), Milstein and co-workers' *trans*-Ru(H)(OH)(CO)(PNN)·*n*H₂O (PNN = (2-(di-*tert*-butylphosphinomethyl)-6-(diethylaminomethyl)pyridine)),⁵ and Whittlesey and co-workers' *cis*-Ru(H)(OH)(CO)₂(IMes)₂ and *cis*-Ru(H)(OH)(CO)(IPr)₂ (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene).¹² The ruthenium-oxygen bond distances for these four compounds fall between 1.995(2) Å and 2.230(2) Å, with the longest Ru-O distances occurring when the hydride is *trans* to the powerful σ -donating hydride ligand. The metal-oxygen bond for **3Ru** is 2.190(2) Å which falls within this range and only slightly shorter than the 2.230(2) Å Ru-O bond distance in Bergman and co-workers' compound (**4**).⁶ Also, the O...O distance between water and hydroxide is shorter for **3Ru** (2.692(4) Å) than in **4** (2.758(3) Å) which indicates a stronger hydrogen bond in our system.

As for structurally characterized Os(H)(OH) complexes, there are two molecular structures reported in the literature: Caulton and co-workers' five coordinate Os(H)(OH)(CO)(P^{*t*}Bu₂Me)₂¹³ and Esteruelas and co-workers' Os(H)(OH)(CO)(η^2 -CH₂=CHCO₂CH₃)(P^{*i*}Pr₃)₂.¹⁴ In both cases, the hydride and hydroxide ligands are *cis* to one another with Os-O bond lengths of 2.022(5) and 2.111(3) Å, respectively, expectedly shorter than the Os-O bond distance of 2.192(3) Å for **3Os** since it is *trans* to a hydride.

Table 3: X-Ray crystal structure and refinement data for complexes **3Ru** and **3Os**.

Compounds	3Ru	3Os
Empirical formula	C ₄₂ H ₅₀ N ₂ O ₂ P ₂ Ru	C ₄₂ H ₅₀ N ₂ O ₂ P ₂ Os
Formula mass	777.85	866.98
Temperature (K)	150(2)	150(1)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	13.9422(4)	13.9210(3)
<i>b</i> (Å)	15.7847(2)	15.8226(4)
<i>c</i> (Å)	16.9683(4)	16.9605(6)
α (°)	90	90
β (°)	94.2440(9)	94.033(2)
γ (°)	90	90
Volume (Å ³)	3724.0(2)	3726.5(2)
<i>Z</i>	4	4
Density (calculated, g/cm ³)	1.387	1.545
Absorption Coefficient (mm ⁻¹)	0.545	3.546
<i>F</i> (000)	1624	1752
Crystal Size (mm ³)	0.14 × 0.12 × 0.06	0.10 × 0.10 × 0.10
Theta range for data collection (°)	2.73–27.56	2.57–27.55
Reflections collected	20367	34052
Independent reflections	8073 [<i>R</i> (<i>int</i>) = 0.0473]	8502 [<i>R</i> (<i>int</i>) = 0.0843]
Completeness to $\theta = 25.00^\circ$ (%)	98.0	98.9
Absorption correction	Multi-scan	Multi-scan
Max. and min. transmission	0.969, 0.882	0.712, 0.577
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	8073/0/449	8502/0/449
Goodness-of-fit on <i>F</i> ²	1.040	1.054
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0461	<i>R</i> ₁ = 0.0428
<i>R</i> indices (all data)	<i>wR</i> ₂ = 0.1268	<i>wR</i> ₂ = 0.0974

3 Conclusion

In summary, we have reacted five coordinate complexes of the general formula $\text{MH}(\text{NHCMe}_2\text{CMe}_2\text{NH}_2)(\text{PPh}_3)_2$ ($\text{M} = \text{Ru}, \text{Os}$) with stoichiometric amounts of water and examined the proton exchange behaviour of the resultant solutions via variable temperature NMR. At low temperatures we were able to observe and spectroscopically characterize the compounds $\text{trans-M}(\text{H})(\text{OH})(\text{NH}_2\text{CMe}_2\text{CMe}_2\text{NH}_2)(\text{PPh}_3)_2 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Ru}, n = 0, 1; \text{M} = \text{Os}, n = 1$) and obtain molecular structures when $n = 1$. Interestingly, the additional molecule of water serves as a hydrogen bonding bridge to a neighbouring metal complex, forming a dimer in the crystal lattice for both Ru and Os. We expect that the proton exchange behaviour observed in these systems would also be relevant for other unsaturated transition metal complexes containing a metal-amido linkage and stoichiometric reactions with water could have implications in characterizing inorganic/organometallic complexes capable of water splitting.

4 Experimental

4.1 General Comments

All experiments were carried out under argon using standard Schlenk and glove box techniques. Compounds $\text{RuH}(\text{NHCMe}_2\text{CMe}_2\text{NH}_2)(\text{PPh}_3)_2$ (**1Ru**)^{8b} and $\text{OsHCl}(\text{NHCMe}_2\text{CMe}_2\text{NH}_2)(\text{PPh}_3)_2$ (**1Os**)^{8d} were synthesized according to known literature procedures. Oxygen-free H_2O was prepared by pouring distilled water into a Schlenk flask, applying high vacuum for about one minute and then sonicating for 10 minutes to remove dissolved gases. The vacuum/sonication steps were repeated twice more after which the vessel was filled with argon. Toluene- d_8 was purchased from Aldrich in individually packaged ampoules and stored in an argon filled glove box over 3 Å molecular sieves before use. D_2O was purchased from Aldrich and degassed prior to use according to the procedure described above and stored under argon. Due to the oxygen sensitivity of the observed products and labile nature of the $\text{OH}/\text{H}_2\text{O}$ moiety, mass spectrometric and elemental analyses were not performed. All NMR

spectroscopic data were collected using a Varian 400 MHz NMR system (operating at 400 MHz for ^1H or 162 MHz for ^{31}P) or an Agilent DD2 600 MHz spectrometer with an Agilent OneNMR probe (operating at 600 MHz for ^1H). All ^1H NMR samples were referenced to their respective residual solvent methyl peak of toluene- d_8 ($\delta = 2.08$) and ^{31}P NMR were referenced to an external standard of 85% aqueous H_3PO_4 at $\delta = 0.00$. Coupling constant J values are given in Hz. For DOSY NMR experiments, Bipolar Pulse Pair Stimulated Echo with Convection Compensation NMR experiment was used.¹⁵ All reactions and spectroscopic experiments were carried out in toluene- d_8 and variable temperature NMR studies were conducted immediately after reacting the metal complexes with water; prolonged exposure of the reaction solutions to low temperatures led to product precipitation or crystallization. Ultraviolet irradiation was conducted using a 450 W Hanovia medium-pressure mercury lamp. Single-crystal X-ray diffraction data were collected at 150 K using a Nonius Kappa-CCD diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The CCD data were integrated and scaled using the Denzo-SMN package.¹⁶ The structures were solved and refined using SHELXTL V6.1.¹⁷ Refinement was by full-matrix least-squares on F^2 using all data.

4.2 **1Ru + H₂O.**

In an argon filled glove box, **1Ru** (20 mg, 0.027 mmol) was placed into an NMR tube and then dissolved in toluene- d_8 (0.8 mL). The tube was sealed with a tight fitting rubber septum which was then wrapped with Parafilm-M[®]. The NMR tube was removed from the glove box and distilled/degassed H_2O (0.50 μL , 0.027 mmol) was injected with a microsyringe. Shaking the tube for a few seconds allowed the droplet of water deposited at the top to react with the **1Ru** solution below and a subsequent change of colour from orange to yellow-orange was observed. The solution was immediately analyzed by NMR spectroscopy. At -40°C , *trans*-Ru(H)(OH)(NH₂CMe₂CMe₂NH₂)(PPh₃)₂ (**2Ru**) is observed. X-ray quality crystals of **3Ru** (vide infra) can be obtained in a few days by leaving the solution sealed and undisturbed at room temperature.. Addition of 3 $\text{\AA}$ molecular sieves at room temperature (before crystallization) generates **1Ru** in

quantitative yield. ^1H NMR (400 MHz; 25 °C): δ_{H} 7.78 (12 H, m, PPh_3), 6.98 (18 H, m, PPh_3), 2.88 (5H, br, $\text{NH}_2 + \text{RuOH}$), 0.88 (12H, s, CH_3), -17.52 (1 H, t, $^2J_{\text{HP}} = 25$ Hz, RuH). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz; 25 °C): δ_{P} 73.05 (s). ^1H NMR (400 MHz; -60 °C): δ_{H} 7.84 (12 H, m, PPh_3), 6.99 (18 H, m, PPh_3), 3.73 (2 H, br, NH_a), 1.95 (2 H, br, NH_b), 0.89 (6 H, s, CH_3), 0.74 (6 H, s, CH_3), -1.51 (1 H, br s, RuOH), -16.88 (1 H, br, RuH). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz; -60 °C): δ_{P} 73.93 (s).

4.3 $1\text{Ru} + 2\text{H}_2\text{O}$.

The same procedure was used as above except two equivalents of distilled/degassed H_2O (1.0 μL , 0.054 mmol) were added to **1Ru** (20 mg, 0.027 mmol) in toluene- d_8 (1.6 mL). The product became yellow after shaking for a few seconds. At -80 °C, *trans*- $\text{Ru}(\text{H})(\text{OH})(\text{NH}_2\text{CMe}_2\text{CMe}_2\text{NH}_2)(\text{PPh}_3)_2 \cdot \text{H}_2\text{O}$ (**3Ru**) is observed. X-ray quality crystals of **3Ru** can be obtained overnight by leaving the solution sealed and undisturbed at room temperature. Addition of 3 Å molecular sieves at room temperature (before crystallization) generates **1Ru** in quantitative yield. ^1H NMR (400 MHz; 25 °C): δ_{H} 7.88–7.77 (12 H, m, PPh_3), 7.03–6.98 (12 H, m, PPh_3), 2.74 (5 H, br, $\text{NH}_a + \text{H}_2\text{O} + \text{RuOH}$), 1.94 (2 H, s, NH_b), 0.95–0.74 (12 H, m, CH_3), -17.51 (1 H, t, $^2J_{\text{HP}} = 25$ Hz, RuH). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz; 25 °C): δ_{P} 72.91 (s). ^1H NMR (400 MHz; -40 °C): δ_{H} 7.93–7.78 (12 H, m, PPh_3), 7.07–6.96 (18 H, m, PPh_3), 3.75 (2 H, br, NH_a), 1.89 (2 H, br, NH_b), 0.95 (6 H, s, CH_3), 0.82 (6 H, s, CH_3), -17.67 (1 H, t, $^2J_{\text{HP}} = 25$ Hz, RuH). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz; -40 °C): δ_{P} 72.45 (s). ^1H NMR (400 MHz; -80 °C): δ_{H} 7.94–7.77 (12 H, m, PPh_3), 7.07–6.99 (18 H, m, PPh_3), 6.48 (2 H, br, partly buried under Ph), H_2O , 3.85 (2 H, br, NH_a), 1.83 (2 H, br, NH_b), 0.94–0.54 (12 H, br, CH_3), -1.24 (1 H, br s, Ru-OH), -17.43 (1 H, br, RuH). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz; -80 °C): δ_{P} 66.70 (s).

4.4 Thermolysis/photolysis of $1\text{Ru} + 2\text{H}_2\text{O}$.

A solution of **3Ru** was prepared as described above. The sample was taken into an argon-filled glove box and transferred via syringe to a J. Young tube. In two independent experiments, the tube was either immersed in a 90 °C oil bath or exposed to

ultraviolet light. The reaction solutions were periodically analyzed by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR. After three days of photolysis, the only observable product by $^{31}\text{P}\{^1\text{H}\}$ NMR is $\text{PPh}_3=\text{O}$; after five days of thermolysis, the only observable products by $^{31}\text{P}\{^1\text{H}\}$ NMR are **3Ru**, PPh_3 , and $\text{PPh}_3=\text{O}$.

4.5 **1Os + $n\text{H}_2\text{O}$ ($n = 1, 2$).**

The same procedure was used as above. When one equivalent of distilled/degassed H_2O (0.5 μL , 0.027 mmol) was to **1Os** (22 mg, 0.027 mmol) in toluene- d_8 (1.1 mL), the solution turned yellow-orange after shaking. At -40°C , both **1Os** and **3Os** are observed a 1:1 ratio. The chemical shifts of **1Os** in toluene- d_8 are nearly identical to those already reported elsewhere in benzene- d_6 .^{8d} When two equivalents of distilled/degassed H_2O (1.0 μL , 0.054 mmol) were added to **1Os** (22 mg, 0.027 mmol) in toluene- d_8 (2.2 mL), the solution turned yellow after shaking. The major observed product by ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR is **3Os**. Addition of 3 Å molecular sieves at room temperature (before crystallization) generates **1Os** in quantitative yield. ^1H NMR (400 MHz; -60°C): δ_{H} 7.78 (12 H, m, PPh_3), 7.06 -6.94 (18 H, m, PPh_3), 6.09 (2 H, br, H_2O), 4.04 (2 H, br, NH_a), 2.43 (2 H, br, NH_b), 0.83-0.70 (12 H, m, CH_3), -0.72 (1 H, br s, OsOH), -19.02 (1 H, br, OsH). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz; -60°C): δ_{P} 22.22 (s).

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6 Supporting Information Available

^1H NMR spectra of **2Ru**, **3Ru** and **3Os** are provided. The Crystallographic Information File (CIF) contains all data for **3Ru** and **3Os**.

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