The useful properties of H_2O as a ligand of a hydrogenase mimic†

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This paper investigates the required properties of Ru-coordinated ligands of a Ni–Ru based hydrogenase mimic. A series of ligands, including MeCN, pyridine, H_2O and OH^- were coordinated to Ru, with H_2O being the only ligand to promote H_2-activation. In addition, a tethered pyridyl moiety was synthesised and found to completely inhibit H_2-activation. We conclude, therefore, that H_2O is the ideal ligand for this mimic as a result of both its mild basicity and the availability of two lone pairs for simultaneous binding to Ru and H_2.

Introduction

Complexes capable of inducing the heterolytic splitting of H_2 into protons and hydride ions are becoming ever more important as hydrogen may become the replacement for fossil fuels.[1-7] The most effective of such complexes are found in naturally occurring enzymes known as hydrogenases and are based around homometallic FeFe cores or heterometallic NiFe cores and it is here that most research has been concentrated.[8-12]

In this laboratory, we have recently successfully synthesised a catalytically active hydrogenase mimic, based on a water-soluble $Ni^{II}Ru^{II}$ aqua complex $\{[\mathbf{A}_{aqua}](NO_3)_2\}$, to induce the heterolytic splitting of H_2 (Fig. 1).[13a] Water appears to play a crucial role in the initial heterolytic splitting of H_2.[4g,4o] Furthermore, we were able to show that the catalyst proceeded through its cycle *via* the following steps: initial coordination of H_2; subsequent H_2O-mediated heterolytic splitting; production of a water-soluble $Ni^{II}Ru^{II}$ hydride complex $\{[\mathbf{B}](NO_3)\}$ with loss of H^+; coordination of a second H_2 molecule with a second heterolytic splitting; reductive elimination of both 'hydrides' to yield both H_2 and a unique, low-valent $Ni^{I}Ru^{I}$ complex and, finally, oxidation of the $Ni^{I}Ru^{I}$ complex to return to the initial $Ni^{II}Ru^{II}$ stage. Over the course of the cycle, two electrons are liberated from two molecules of hydrogen.[13]

A crucial step in this mechanism is the coordination of H_2 to the metal centre with a subsequent nucleophilic attack by the H_2O ligand to heterolytically activate the H–H bond, as shown in Fig. 1.[14,15] This step results in a hydride coordinated to the $Ni^{II}Ru^{II}$ centre and H_3O^+ as a leaving group to carry away the complementary proton. In short, H_2O appears to play a crucial role in the initial heterolytic splitting of H_2. This conclusion is supported by the presence of an oxygen-bearing ligand in natural hydrogenases, which we have proposed must also be H_2O. For these reasons, we wished to study the role of the H_2O ligand in more detail and therefore investigated the possibility of replacing water with other ligands.

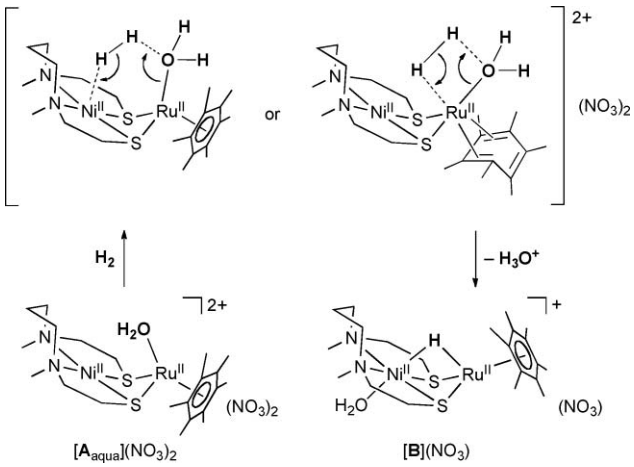

Fig. 1 A Ni–Ru based hydrogenase mimic, based on a $Ni^{II}Ru^{II}$ aqua complex $\{[\mathbf{A}_{aqua}](NO_3)_2\}$, to induce the proposed heterolytic splitting of H_2 and produce a $Ni^{II}Ru^{II}$ hydride complex $\{[\mathbf{B}](NO_3)\}$.

We suspected that a crucial advantage of H_2O in this context would be its Lewis basicity, or pK_a. Ligands with a high pK_a value would bind too strongly to the metal centres, whereas ligands that are too weak would be unable to heterolytically activate H_2. Accordingly, we initiated a study of Ru-coordinated ligands, with varying basicity and binding mode. Having previously reported experiments in the presence of the weak base MeCN,[16] we extended our research to investigate stronger bases such as pyridine and hydroxide ion. Furthermore, we synthesised $[Ni^{II}(\mu\text{-}SR)_2Ru^{II}(Bz\wedge py)](BF_4)_2$ $[\mathbf{3}](BF_4)_2$, $(\mu\text{-}SR)_2$ = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-mercaptoethyl)-1,3-propanediamine, Bz∧py = 2-(pentamethylbenzyl)pyridine} to investigate the difference between inter- and intramolecular binding of analogous ligands.

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† Electronic supplementary information (ESI) available: Electrospray ionisation mass spectra of **1** (Fig. S1) and $[\mathbf{2}](BF_4)_2$ (Fig. S3) and IR spectra of **1** (Fig. S2), $[\mathbf{2}](BF_4)_2$ (Fig. S4) and $[\mathbf{3}](BF_4)_2$ (Fig. S5) as KBr disks, UV-vis spectral change for the reaction of $[\mathbf{A}_{aqua}](NO_3)_2$ with H_2 (Fig. S6) and pH titration of Bz∧py (Fig. S7). CCDC reference numbers 749758–749760. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b921273f

Experimental

Materials and methods

All experiments were carried out under a N_2 or an Ar atmosphere using standard Schlenk techniques and a glovebox. The manipulations in the acidic media were carried out with plasticware (without metals). Distilled water, 0.1 M NaOH and 0.1 M HNO_3 were purchased from Wako Pure Chemical Industries, Ltd. and D_2O (99.9% D) was purchased from Cambridge Isotope Laboratories, Inc.; these reagents were used as received. H_2 gas (99.9999%) was purchased from Taiyo Toyo Sanso Co., Ltd. Other chemicals (highest purity available) were purchased from Aldrich Chemicals Co. and used without further purification. A Ni^{II} complex $[Ni^{II}(SR)_2]$ {$(SR)_2$ = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-mercaptoethyl)-1,3-propanediamine},[17] the $Ni^{II}Ru^{II}$ aqua complex $[Ni^{II}(\mu\text{-}SR)_2Ru^{II}(H_2O)(\eta^6\text{-}C_6Me_6)](NO_3)_2$ {$[\mathbf{A}_{aqua}](NO_3)_2$}[13] and the $Ni^{II}Ru^{II}$ hydride complex $[Ni^{II}(\mu\text{-}SR)_2(H_2O)(\mu\text{-}H)Ru^{II}(\eta^6\text{-}C_6Me_6)](NO_3)$ {$[\mathbf{B}](NO_3)$}[13] were prepared by the methods described in the literatures.

The ^{1}H NMR spectra were recorded on a JEOL JNM-AL 300 spectrometer at 25 °C. ^{1}H NMR experiments in D_2O and $CDCl_3$ were measured using 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt (TSP) and tetramethylsilane (TMS) as an internal standard, respectively. Electrospray ionisation mass spectrometry (ESI-MS) data were obtained by a JEOL JMS-T100LC and an API 365 triple-quadrupole mass spectrometer (PE-Sciex). IR spectra of solid compounds in KBr disks were recorded on a Thermo Nicolet NEXUS 8700 FT-IR instrument from 650 to 4000 cm^{-1} using 2 cm^{-1} standard resolution. UV-visible spectra were recorded on a JASCO V-670 UV-Visible-NIR spectrophotometer and an Otsuka MCPD-2000 spectrometer.

The pH of the solution was adjusted by using 0.1 M HNO_3/H_2O and 0.1 M $NaOH/H_2O$. In a pH range of 2.0-11.0, the pH of the solution was determined by a pH meter (TOA: HM-5A) equipped with a glass electrode (TOA: GS-5015C). pD values were corrected by adding 0.4 to the observed values (pD = pH meter reading + 0.4).[18]

2-(Pentamethylbenzyl)pyridine (Bz∧py)

To a solution of 2-bromopyridine (1.1 g, 7.1 mmol) in tetrahydrofuran (10 mL) under N_2 was added a solution of *n*-BuLi (1.6 M in n-hexane, 3.6 mL, 5.7 mmol) dropwise over 10 min at −78 °C. After stirring for 15 min, a solution of pentamethylbenzaldehyde (500 mg, 2.8 mmol) in tetrahydrofuran (4.0 mL) was added to the reaction mixture. The resulting solution was stirred at −78 °C for 1 h and then allowed to warm to 25 °C. After addition of a Na_2CO_3-saturated aqueous solution (20 mL), the mixture was extracted with dichloromethane. The combined organic layers were washed with water. The extract was dried over anhydrous $MgSO_4$, filtered and concentrated to yield an oil. The oil was purified by flash column chromatography on silica gel eluted with n-hexane–ethyl acetate (9/1). Into a 50 mL flask were charged the oil and red phosphorus (320 mg, 10 mmol), and 47% HI (15 mL) was added. The mixture was vigorously refluxed for 15 h. The cooled reaction mixture was diluted with a Na_2CO_3-saturated aqueous solution until basic. The deposited product was dissolved with dichloromethane and the mixture was filtered through celite to remove phosphorus. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with water, dried over $MgSO_4$ and concentrated. The product was purified by flash column chromatography on silica gel eluted with n-hexane–ethyl acetate (9/1) and recrystallised from dichloromethane–n-hexane to give pure 2-(pentamethylbenzyl)pyridine (550 mg, 90% based on pentamethylbenzaldehyde). FT-IR (cm^{-1}, KBr disk): 2921 (aliphatic C–H), 1586 (aromatic C=C or C=N), 1566 (aromatic C=C or C=N), 1474 (aromatic C=C or C=N), 1428 (aromatic C=C or C=N), 749. ^{1}H NMR (in $CDCl_3$, reference to TMS, 25 °C): δ 2.18 {s, 6H, $C_6(CH_3)_5$}, 2.24 {s, 6H, $C_6(CH_3)_5$}, 2.27 {s, 3H, $C_6(CH_3)_5$}, 4.31 (s, 2H, -CH_2-), 6.77 (d, ^3J = 7.8 Hz, 1H, NC_5H_4), 7.06 (m, ^3J = 7.6 Hz, 1H, NC_5H_4), 7.47 (t, ^3J = 7.4 Hz, 1H, NC_5H_4), 8.56 (d, ^3J = 7.5 Hz, 1H, NC_5H_4).

$[Ru^{II}(Bz\wedge py)Cl_2]$ (1)

In a 300 mL flask were placed $Ru^{III}Cl_3{\cdot}3H_2O$ (1.3 g, 5.0 mmol), molecular sieves 4A (40 g), 1,2-dichloroethane (100 mL) and ethanol (10 mL). The solution was stirred at ambient temperature for 30 min, and then Bz∧py was added (1.3 g, 5.5 mmol). The reaction solution was stirred at 80 °C for 48 h. The reaction solution was filtered and the solvent was removed under reduced pressure to yield a crude product of **1** (yield 44% based on $Ru^{III}Cl_3{\cdot}3H_2O$). Orange crystals of **1** were obtained from a dichloromethane–n-hexane solution. FT-IR (cm^{-1}, KBr disk): 3099 (aliphatic C–H), 3068 (aliphatic C–H), 3020 (aliphatic C–H), 2925 (aliphatic C–H), 1600 (aromatic C=C or C=N), 1440 (aromatic C=C or C=N), 1383 (aromatic C=C or C=N), 1325 (aromatic C=C or C=N), 1250, 1194, 1161, 1070, 1055, 1024, 1005, 910, 818, 785, 769. ^{1}H NMR (in $CDCl_3$, reference to TMS, 25 °C): δ 2.10 {s, 6H, $C_6(CH_3)_5$}, 2.13 {s, 3H, $C_6(CH_3)_5$}, 2.15 {s, 6H, $C_6(CH_3)_5$}, 4.38 (s, 2H, -CH_2-), 7.19 (t, ^3J = 7.5 Hz, 1H, NC_5H_4), 7.36 (d, ^3J = 7.2 Hz, 1H, NC_5H_4), 7.73 (t, ^3J = 7.5 Hz, 1H, NC_5H_4), 8.24 (d, ^3J = 7.5 Hz, 1H, NC_5H_4). ESI-MS (in MeOH): m/z 376.1 {$[\mathbf{1} - Cl]^+$; relative intensity (I) = 100% in the range of m/z 100-2000}. Anal. Calcd for **1**: $C_{17}H_{21}NCl_2Ru$: C, 49.64; H, 5.15; N, 3.41%. Found: C, 49.82; H, 4.78; N, 3.46%.

$[Ru^{II}(Bz\wedge py)(H_2O)_2](BF_4)_2$ {[2](BF$_4$)$_2$}

A solution of **1** (820 mg, 2.0 mmol) and $AgBF_4$ (780 mg, 4.0 mmol) in water (20 mL) at pH 7.0 was stirred at 25 °C for 6 h under N_2 and the precipitating AgCl was removed by filtration. The solvent was evaporated to yield a yellow moisture sensitive powder of [**2**](BF$_4$)$_2$, which was dried *in vacuo* (yield 95% based on **1**). Brown crystals of [**2**](BF$_4$)$_2$ were obtained from a dichloromethane–n-hexane solution. FT-IR (cm^{-1}, KBr disk): 3450 (O–H), 3097 (aliphatic C–H), 3068 (aliphatic C–H), 3057 (aliphatic C–H), 3018 (aliphatic C–H), 2966 (aliphatic C–H), 2935 (aliphatic C–H), 1605 (aromatic C=C or C=N), 1560 (aromatic C=C or C=N), 1444 (aromatic C=C or C=N), 1384 (aromatic C=C or C=N), 1056 (BF_4), 784, 769. ^{1}H NMR (in D_2O at pD 7.0, reference to TSP, 25 °C): δ 2.08 {s, 6H, $C_6(CH_3)_5$}, 2.17 {s, 6H, $C_6(CH_3)_5$}, 2.27 {s, 3H, $C_6(CH_3)_5$}, 4.73 (s, 2H, -CH_2-), 7.20 (d, ^3J = 5.1 Hz, 1H, NC_5H_4), 7.39 (t, ^3J = 7.2 Hz, 1H, NC_5H_4), 7.78 (d, ^3J = 8.1,Hz, 1H, NC_5H_4), 8.09 (t, ^3J = 7.8 Hz, 1H, NC_5H_4). ESI-MS (in MeOH): m/z 376.6 ([**2** − H]$^+$; I = 35% in the range of m/z 100-2000). Anal. Calcd for

[**2**](PF$_6$)$_2$: $C_{17}H_{25}NF_{12}O_2P_2Ru$: C, 30.64; H, 3.78; N, 2.10%. Found: C, 30.33; H, 4.07; N, 2.12%.

[Ni^{II}(μ-SR)$_2$Ru^{II}(Bz∧py)](BF$_4$)$_2$ {[**3**](BF$_4$)$_2$}

A solution of [**2**](BF$_4$)$_2$ (0.30 g, 0.60 mmol) in water (20 mL) at pH 7.0 was added to a solution of the Ni^{II} complex [Ni^{II}(SR)$_2$] (0.17 g, 0.60 mmol) in water (20 mL) at pH 7.0. The solution was stirred at 25 °C. After 4 h, the solvent was evaporated to yield a brown powder of [**3**](BF$_4$)$_2$, which was dried *in vacuo* {72% isolated yield based on [**2**](BF$_4$)$_2$}. Recrystallisation of [**3**](BF$_4$)$_2$ from a dichloromethane–n-hexane solution gave orange crystals that were suitable for X-ray analysis. FT-IR (cm^{-1}, KBr disk): 2933 (aliphatic C–H), 1633 (aromatic C=C or C=N), 1603 (aromatic C=C or C=N), 1564 (aromatic C=C or C=N), 1460 (aromatic C=C or C=N), 1437 (aromatic C=C or C=N), 1389 (aromatic C=C or C=N), 1055 (BF$_4$), 789, 775, 748. ^{1}H NMR (in D$_2$O at pD 7.0, reference to TSP, 25 °C): δ 1.67-1.89, 2.02-2.04, 2.12-2.19, 2.42-2.44, 2.76-2.81 and 3.16-3.40 (m, 14H, -CH_2-), 2.23 {s, 6H, C$_6$(CH_3)$_5$}, 2.49 {s, 6H, C$_6$(CH_3)$_5$}, 2.71 {s, 3H, C$_6$(CH_3)$_5$}, 2.86 (s, 6H, N–CH_3), 4.57 (s, 2H, -CH_2-), 7.16 (d, ^3J = 7.5 Hz, 1H, NC$_5H_4$), 7.35 (t, ^3J = 7.2 Hz, 1H, NC$_5H_4$), 7.53 (d, ^3J = 7.8 Hz, 1H, NC$_5H_4$), 7.89 (t, ^3J = 7.5 Hz, 1H, NC$_5H_4$). ESI-MS (in MeOH): *m*/*z* 309.6 {[**3**]$^{2+}$; *I* = 100% in the range of *m*/*z* 100-2000}. Anal. Calcd for [**3**](BF$_4$)$_2$·H$_2$O: $C_{26}H_{43}N_3B_2F_8NiORuS_2$: C, 38.50; H, 5.34; N, 5.18%. Found: C, 38.79; H, 5.24; N, 5.33%.

Procedure for the titration of bases to a Ni^{II}Ru^{II} aqua complex [Ni^{II}(μ-SR)$_2$Ru^{II}(H$_2$O)(η^6-C$_6$Me$_6$)](NO$_3$)$_2$ {[A_{aqua}](NO$_3$)$_2$}

To aqueous solutions of a Ni^{II}Ru^{II} aqua complex {[A_{aqua}](NO$_3$)$_2$} (0.1 mM), were added increasing equivalents of MeCN and pyridine, respectively. The pH of the resulting solutions were adjusted by using 0.1 M HNO$_3$/H$_2$O and 0.1 M NaOH/H$_2$O to pH 7.0. H$_2$ gas was bubbled through the resulting solutions for 10 min. The yields of a Ni^{II}Ru^{II} hydride complex [Ni^{II}(μ-SR)$_2$(H$_2$O)(μ-H)Ru^{II}(η^6-C$_6$Me$_6$)](NO$_3$) {[**B**](NO$_3$)} were determined by UV-vis spectroscopy.

X-ray crystallographic analysis

Crystallographic data for **1**, [**2**](BF$_4$)$_2$ and [**3**](BF$_4$)$_2$ have been deposited with the Cambridge Crystallographic Data Center (CCDC reference numbers 749758–749760).† Measurements were made on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.7107 Å) and Rigaku/MSC Saturn CCD diffractometer with confocal monochromated Mo-Kα radiation (λ = 0.7107 Å). Data were collected and processed using the teXsan crystallographic software package of Molecular Structure Corporation.

Results and discussion

A new ligand, Bz∧py

A new 2-(pentamethylbenzyl)pyridine (Bz∧py) ligand was designed to prepare a Ru^{II} centre having simultaneous Ru^{II}-(η^6-C$_6$Me$_5$) and Ru^{II}-(NC$_5$H$_4$) bonds with potentially two vacant coordination sites on the metal centre. In aqueous media, these vacant coordination sites should be occupied by two H$_2$O molecules. Bz∧py was synthesised from pentamethylphenyl(2-pyridyl)methanol, which was itself prepared by the reaction of 2-bromopyridine with pentamethylbenzaldehyde (see Experimental).

Synthesis and structure of [Ru^{II}(Bz∧py)Cl$_2$] (1)

A dichloro Ru^{II} complex [Ru^{II}(Bz∧py)Cl$_2$] (**1**) was prepared by the reaction of Ru^{III}Cl$_3$·3H$_2$O with Bz∧py in a mixed solvent of 1,2-dichloroethane–ethanol (Fig. 2). It should be noted that the pyridyl moiety induces a significant intramolecular templating effect. Previous syntheses of analogous Ru^{II}-(η^6-C$_6$Me$_5$) complexes required initial treatment of Ru^{III}Cl$_3$ with *p*-mentha-1,5-diene to produce a reactive intermediate, [Ru^{II}Cl$_2$(η^6-*p*-MeC$_6$H$_4$CHMe$_2$)]$_2$, that could be converted to the Ru^{II}-(η^6-C$_6$Me$_5$) complex at high temperatures.[19] In this case, however, **1** could be formed directly in refluxing 1,2-dichloroethane–ethanol.

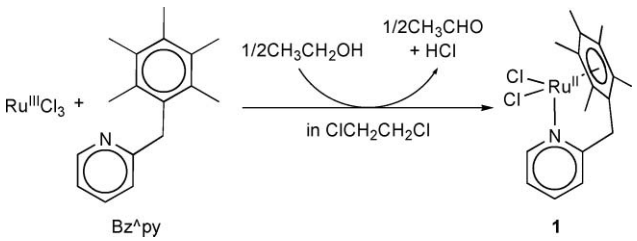

Fig. 2 Synthesis of **1**.

The structure of **1** was determined by X-ray analysis, as shown in Fig. 3. Complex **1** adopts a distorted-octahedral coordination with two perpendicular planes {the torsion angle between the least-squares plane of η^6-C$_6$Me$_5$ and that of NC$_5$H$_4$ = 98.67(8) °} as a result of the formation of the expected Ru^{II}-(η^6-C$_6$Me$_5$) and Ru^{II}-(NC$_5$H$_4$) bonds.

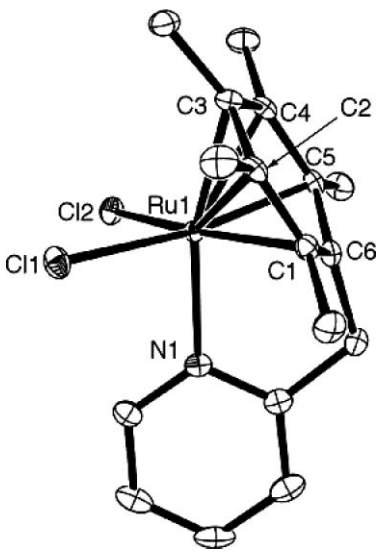

Fig. 3 An ORTEP drawing of **1** with ellipsoids at 50% probability. The hydrogen atoms are omitted for clarity. Selected interatomic distances (*l*/Å) and angles (ϕ/°): Ru1-Cl1 = 2.400(1), Ru1-Cl2 = 2.420(1), Ru1-N1 = 2.124(2), Ru1-C1 = 2.184(2), Ru1-C2 = 2.220(2), Ru1-C3 = 2.192(2), Ru1-C4 = 2.210(2), Ru1-C5 = 2.173(2), Ru1-C6 = 2.086(2), Cl1-Ru1-Cl2 = 90.62(2), Cl1-Ru1-N1 = 88.31(6), Cl2-Ru1-N1 = 86.88(5).

The dichloro Ru^{II} complex **1** was characterised by ^1H NMR spectroscopy in $CDCl_3$ (Fig. 4), electrospray ionisation mass spectrometry (ESI-MS) (Fig. S1 in ESI†), IR spectroscopy (Fig. S2 in ESI†) and elemental analysis. The signals at 7.19 ppm, 7.36 ppm, 7.73 ppm and 8.24 ppm correspond to the pyridine protons of the Bz∧py ligand; the signal observed at 4.38 ppm is derived from the methylene group of the Bz∧py ligand and the signals at 2.10 ppm, 2.13 ppm and 2.15 ppm are derived from the $C_6(CH_3)_5$ group of the Bz∧py ligand.

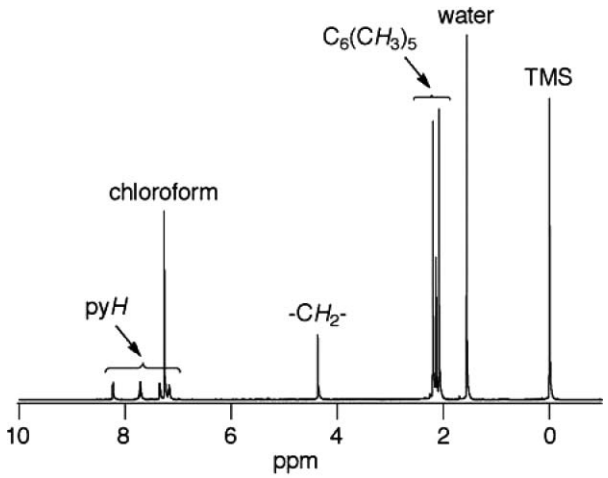

Fig. 4 ^1H NMR spectrum of **1** in $CDCl_3$ at 25 °C. TMS: the reference with the methyl proton resonance set at 0.00 ppm.

Synthesis and structure of $[Ru^{II}(Bz\wedge py)(H_2O)_2](BF_4)_2$ {[2](BF4)2}

Following methods developed in this laboratory,[20] the chloride ions in complex **1** were reacted with 2 equivalents of $AgBF_4$ to yield a diaqua Ru^{II} complex $[Ru^{II}(Bz\wedge py)(H_2O)_2](BF_4)_2$ {[**2**](BF4)2} in water at pH 7.0 (Fig. 5). This complex was characterised by X-ray analysis (Fig. 6), ^1H NMR spectroscopy (Fig. 7), ESI-MS (Fig. S3 in ESI†), IR spectroscopy (Fig. S4 in ESI†) and elemental analysis.

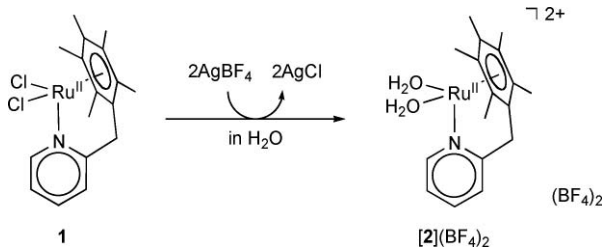

Fig. 5 Synthesis of [**2**](BF4)2.

In the structure determined by X-ray analysis (Fig. 6), all hydrogen atoms were included in the least-squares calculation of [**2**](BF4)2. An ORTEP drawing of [**2**](BF4)2 demonstrates that **2** adopts a distorted-octahedral coordination, surrounded by one Bz∧py and two H_2O ligands.

Fig. 7 shows a ^1H NMR spectrum of the diaqua Ru^{II} complex [**2**](BF4)2 in D_2O at pD 7.0. The signals at 7.20 ppm, 7.39 ppm, 7.78 ppm and 8.09 ppm correspond to the pyridine protons of the Bz∧py ligand; the signal observed at 4.73 ppm is derived from the methylene group of the Bz∧py ligand and the signals at 2.08 ppm,

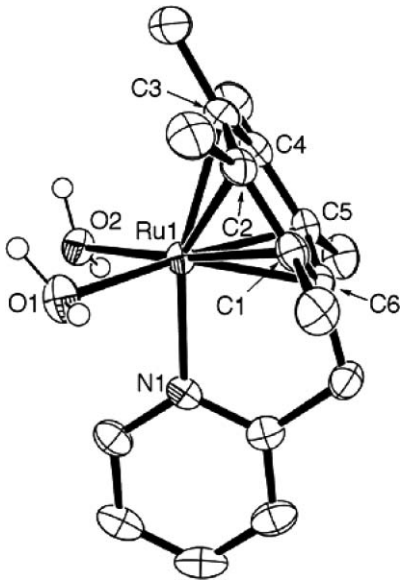

Fig. 6 An ORTEP drawing of [**2**](BF4)2 with ellipsoids at 50% probability. The counter anions (BF_4) and hydrogen atoms of Bz∧py are omitted for clarity. Selected interatomic distances (l/Å) and angles (ϕ/°): Ru1-O1 = 2.146(2), Ru1-O2 = 2.157(2), Ru1-N1 = 2.092(3), Ru1-C1 = 2.179(3), Ru1-C2 = 2.188(3), Ru1-C3 = 2.234(3), Ru1-C4 = 2.194(3), Ru1-C5 = 2.183(3), Ru1-C6 = 2.092(3), O1-Ru1-O2 = 79.42(9), O1-Ru1-N1 = 83.7(1), O2-Ru1-N1 = 86.5(1).

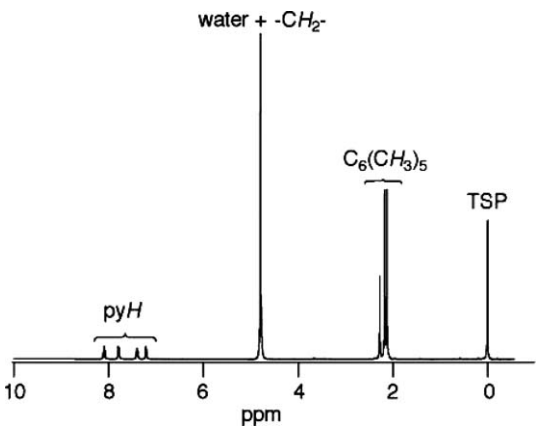

Fig. 7 ^1H NMR spectrum of [**2**](BF4)2 in D_2O at pD 7.0 at 25 °C. TSP: the reference with the methyl proton resonance set at 0.00 ppm.

2.17 ppm and 2.27 ppm are derived from the $C_6(CH_3)_5$ group of the Bz∧py ligand.

Synthesis and structure of the dinuclear $Ni^{II}Ru^{II}$ complex $[Ni^{II}(\mu\text{-}SR)_2Ru^{II}(Bz\wedge py)](BF_4)_2$ {[3](BF4)2}

We obtained a water-soluble $Ni^{II}Ru^{II}$ complex $[Ni^{II}(\mu\text{-}SR)_2Ru^{II}(Bz\wedge py)](BF_4)_2$ {[**3**](BF4)2} by the reaction of the diaqua Ru^{II} complex [**2**](BF4)2 with the Ni^{II} complex $[Ni^{II}(SR)_2]$ in water at pH 7.0 (Fig. 8).

The structure of [**3**](BF4)2 was characterised by IR spectroscopy (Fig. S5 in ESI†), X-ray analysis (Fig. 9), ^1H NMR spectroscopy (Fig. 10), ESI-MS (Fig. 11) and elemental analysis. X-ray analysis was performed on an orange crystal of [**3**](BF4)2, obtained from a dichloromethane–n-hexane solvent mixture. Fig. 9 shows that the

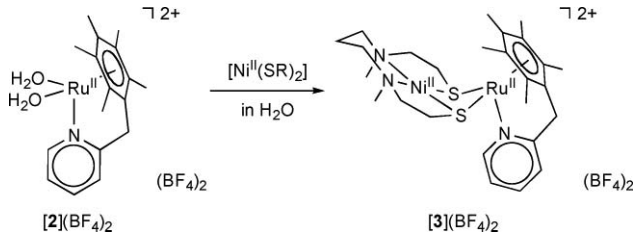

Fig. 8 Synthesis of $[\mathbf{3}](BF_4)_2$.

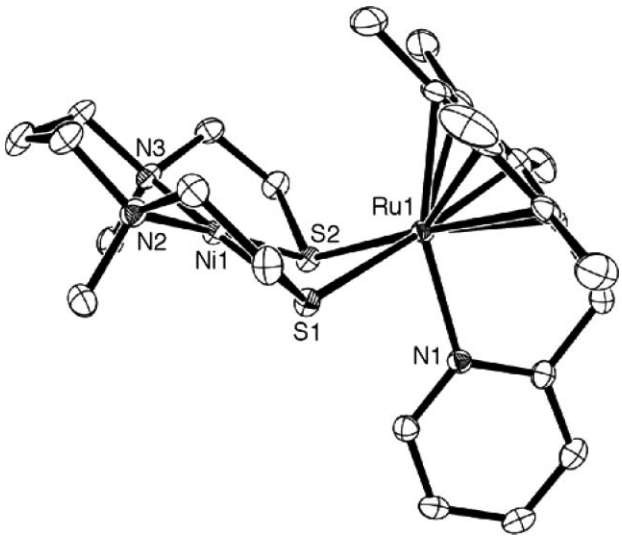

Fig. 9 An ORTEP drawing of $[\mathbf{3}](BF_4)_2$ with ellipsoids at 50% probability. The counter anions (BF_4) and hydrogen atoms are omitted for clarity. Selected interatomic distances (l/Å) and angles (ϕ/°): Ru1-S1 = 2.421(1), Ru1-S2 = 2.422(1), Ru1-N1 = 2.173(2), Ni1-S1 = 2.172(1), Ni1-S2 = 2.180(1), Ni1-N2 = 1.976(2), Ni1-N3 = 1.967(2), Ni1-S1-Ru1 = 88.90(2), Ni1-S2-Ru1 = 88.67(2).

structure of **3** contains a NiS_2Ru butterfly core, in which the Ni atom and the Ru atom are linked by two thiolato units of SR. The Ni1-S1-Ru1 and Ni1-S2-Ru1 angles are 88.90(2) and 88.67(2)°, respectively. The Ni atom of **3** adopts a square planar geometry with a SR ligand, whereas the Ru atom of **3** adopts a distorted-octahedral coordination which is surrounded by one Bz∧py and the metalloligand $[Ni^{II}(SR)_2]$.

Fig. 10 shows a ^{1}H NMR spectrum of the $Ni^{II}Ru^{II}$ complex $[\mathbf{3}](BF_4)_2$ in D_2O at pD 7.0. The signals at 7.16 ppm, 7.35 ppm, 7.53 ppm and 7.89 ppm correspond to the pyridine protons of the Bz∧py ligand; the signal observed at 4.57 ppm is derived from the methylene group of the Bz∧py ligand; the signals at 2.23 ppm, 2.49 ppm and 2.71 ppm are derived from the $C_6(CH_3)_5$ group of the Bz∧py ligand, the signal at 2.86 ppm corresponds to the methyl protons bound to the N atoms and the signals at 1.67-1.89 ppm, 2.02-2.04 ppm, 2.12-2.19 ppm, 2.42-2.44 ppm and 3.16-3.40 ppm are derived from the methylene group of the metalloligand $[Ni^{II}(SR)_2]$ of **3**.

Fig. 11a shows a positive-ion ESI mass spectrum of $[\mathbf{3}](BF_4)_2$ in methanol. The prominent signal at m/z 309.6 {relative intensity (I) = 100% in the range of m/z 100-2000} has a characteristic distribution of isotopomers (Fig. 11b) that matches well with the calculated isotopic distribution for $[\mathbf{3}]^{2+}$ (Fig. 11c).

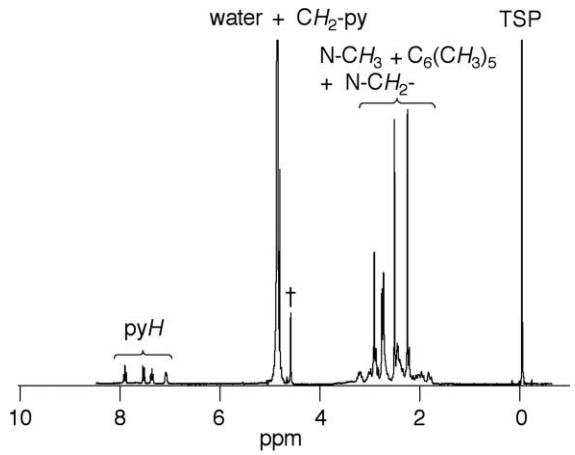

Fig. 10 ^{1}H NMR spectrum of $[\mathbf{3}](BF_4)_2$ in D_2O at pD 7.0 at 25 °C. TSP: the reference with the methyl proton resonance set at 0.00 ppm. †: the protons of dichloromethane which was used to recrystallise $[\mathbf{3}](BF_4)_2$.

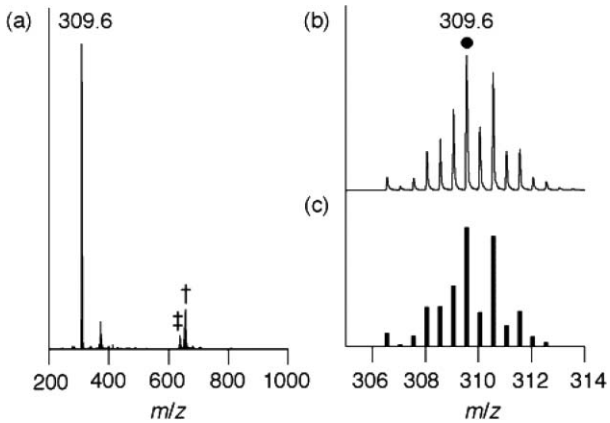

Fig. 11 (a) Positive-ion ESI mass spectrum of $[\mathbf{3}](BF_4)_2$ in methanol. (b) Signal at m/z 309.6 for $[\mathbf{3}]^{2+}$. (c) Calculated isotopic distribution for $[\mathbf{3}]^{2+}$. †: the signal of $\{[\mathbf{3} + Cl]^+\}$. ‡: the signal of $\{[\mathbf{3} + F]^+\}$.

The effects of changing Ru-ligand basicity

As previously reported, completely replacing H_2O with MeCN to form $[Ni^{II}(\mu\text{-}SR)_2Ru^{II}(MeCN)(\eta^6\text{-}C_6Me_6)](NO_3)_2$ in 100% MeCN renders the complex inactive.[16] Subsequently, however, we considered that titration experiments would prove more informative and thus we performed a series of such measurements, utilising several different possible ligands. These experiments were intended to investigate how changing the Ru-coordinated ligand would enhance or inhibit the heterolytic splitting of H_2 by $[\mathbf{A}_{aqua}](NO_3)_2$ to form $[\mathbf{B}](NO_3)$.

The results of titrating $[\mathbf{A}_{aqua}](NO_3)_2$ with MeCN are shown in Fig. 12 (closed circle). Clearly, MeCN has an inhibitory effect on the action of $[\mathbf{A}_{aqua}](NO_3)_2$,—in an aqueous solution, the addition of 100 equivalents of MeCN reduces the production of $[\mathbf{B}](NO_3)$ from 100% to around 45%. Whilst MeCN is capable of inhibiting the action of $[\mathbf{A}_{aqua}](NO_3)_2$, it cannot shut it down completely, and this observation is supported by previous experiments which showed that adding water to the MeCN-coordinated complex in an MeCN solution revives the H_2 splitting activity.

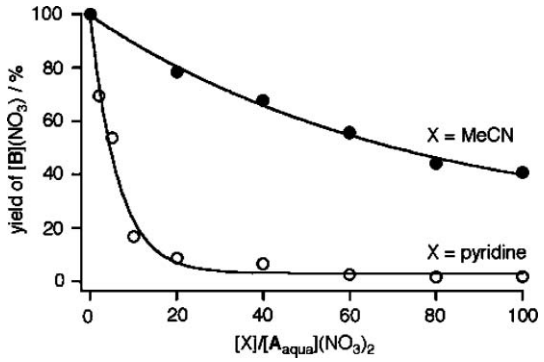

Fig. 12 A correlation between the equivalent of X {MeCN (closed circle) or pyridine (open circle) to $[\mathbf{A}_{aqua}](NO_3)_2$} and the yield of $[\mathbf{B}](NO_3)$ in water at pH 7.0 at 25 °C.

We considered the inhibitory activity of MeCN to be the result of its ability to displace H_2O as a ligand. Since MeCN has only one lone pair available for coordination, it cannot simultaneously bind to Ru and H_2, thereby rendering the complex inert to H_2. If this is the case, N-based ligands with a higher pK_a should have a stronger inhibitory effect as they are less likely to be displaced by H_2O.

This conclusion was borne out by titration experiments with pyridine (open circle in Fig. 12). Only 2 equivalents of pyridine was able to reduce the yield of hydride species from 100% to 70%. This inhibition continued steadily, reducing the yield to 15% at 10 equivalents and finally reaching 0% yield at around 60 equivalents of pyridine. Clearly, the stronger basicity of pyridine completely blocks the Ru^{II} centre from encroaching H_2O ligand, effectively poisoning the potential catalyst.

In order to confirm our proposals regarding the action of pyridine, we attached a pyridine moiety directly to the hexamethylbenzene ligand. This arrangement was expected to direct the binding of the pyridine moiety exclusively to the Ru^{II} centre, increasing the *effective* molarity of the pyridine whilst only incorporating one equivalent of pyridine moiety with respect to Ru. Indeed, this modification rendered the complex completely inert to H_2 in water in a range of pH 2.0-11.0 (Fig. 13), confirming that coordination to Ru is responsible for inhibition, rather than simply adding base.

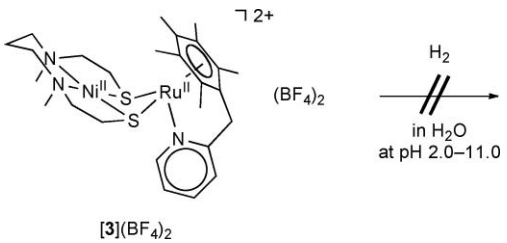

Fig. 13 Reaction of **3** with H_2 in water at pH 2.0-11.0.

Taking the series further, we deprotonated the Ru-coordinated H_2O of $[\mathbf{A}_{aqua}](NO_3)_2$ to form the hydroxo complex $[Ni^{II}(\mu\text{-}SR)_2Ru^{II}(OH)(\eta^6\text{-}C_6Me_6)](NO_3)$ $\{[\mathbf{A}_{hydroxo}](NO_3)\}$ above pH 8.4 (Fig. 14).[21] This change leaves the oxygen in place, now with *three* lone pairs, but it significantly increases the basicity of the ligand and results in a concomitant reduction in lability. Subsequent experiments showed that the hydroxo complex $[\mathbf{A}_{hydroxo}](NO_3)$ was

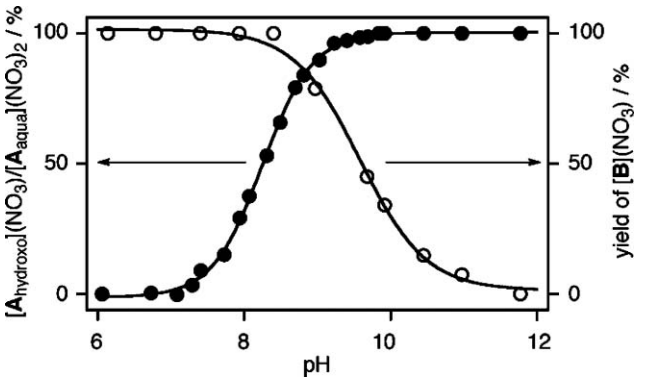

Fig. 14 pH-dependent ratio of $[\mathbf{A}_{aqua}](NO_3)_2$ and $[\mathbf{A}_{hydroxo}](NO_3)$ in water (closed circle). The titration of an aqueous solution of $[\mathbf{A}_{aqua}](NO_3)_2$ (100 μM) with 0.1 M NaOH and 0.1 M HNO_3 under an Ar atmosphere was performed, which was monitored by UV-vis spectroscopy. pH-dependent yields of $[\mathbf{B}](NO_3)$ from the reaction of $[\mathbf{A}_{aqua}](NO_3)_2$ with H_2 in water (open circle).

completely unable to form a hydride, indeed, the titration curve for deprotonation (closed circle in Fig. 14) is the direct inverse of the curve for H_2-activation (open circle in Fig. 14). Therefore, we conclude that the ability to coordinate to H_2 is not enough to induce heterolytic splitting—there is also a need for a labile H_3O^+ ion as a leaving group.[22]

Complex $[\mathbf{A}_X](NO_3)_n$ {X = MeCN ($n = 2$), pyridine ($n = 2$) or OH^- ($n = 1$)} was unreactive toward H_2 in water at pH 7.0 at 25 °C (Fig. 15). In contrast, the reaction of $[\mathbf{A}_{aqua}](NO_3)_2$ with H_2 in water at pH 7.0 at 25 °C obeyed first-order kinetics ($v = k_{obs}[\mathbf{A}_{aqua}]$) under a H_2 atmosphere. The rate constant k_{obs} was determined as 2.7×10^{-3} s^{-1} by UV-vis spectroscopy (Fig. S6 in ESI†).

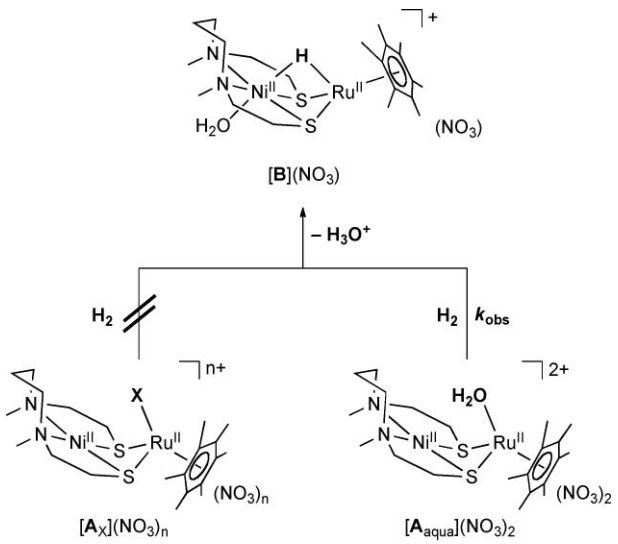

Fig. 15 Reactivity of $[\mathbf{A}_X](NO_3)_n$ {X = MeCN ($n = 2$), pyridine ($n = 2$) or OH^- ($n = 1$)} and $[\mathbf{A}_{aqua}](NO_3)_2$ toward H_2.

Fig. 16 summarises the properties of the Ru^{II}-coordinated ligands investigated in this study with reference to the Lewis basicity of the ligand and availability of lone pairs for binding.

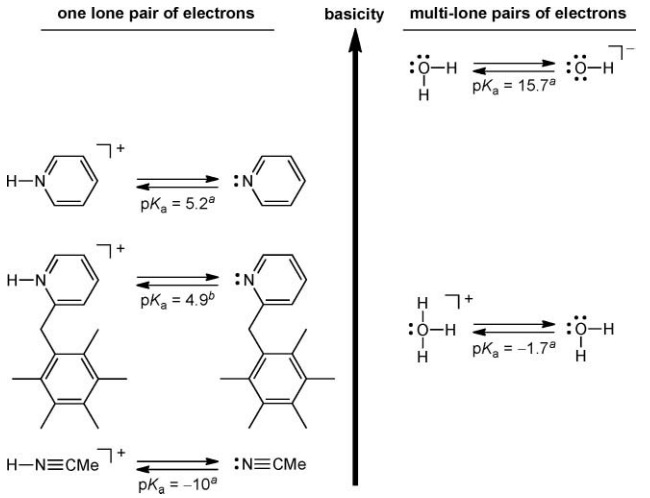

Fig. 16 Ru^{II}-coordinated ligands investigated in this study. [a] ref. 23. [b] pK_a value was determined by titration (see Fig. S7 in ESI†).

Conclusions

This study has shown that H_2O is an ideal ligand for Ru-coordination based on both its pK_a and electronic properties. Ligands immediately either side in terms of pK_a, but only bearing one lone pair were not able to promote H_2 activation. Furthermore, the HO^- ligand, whilst bearing three lone pairs, was also unable to promote H_2-activation. These studies also support our proposal that the oxygen-bearing ligand at the centre of natural hydrogenases is H_2O.

Acknowledgements

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