pH-Dependent isotope exchange and hydrogenation catalysed by water-soluble NiRu complexes as functional models for [NiFe]hydrogenases†

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The pH-dependent hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes and hydrogenation of the carbonyl compounds have been investigated with water-soluble bis(μ-thiolate)(μ-hydride)NiRu complexes, $Ni^{II}(\mu\text{-}SR)_2(\mu\text{-}H)Ru^{II}$ $\{(\mu\text{-}SR)_2 =$ *N*,*N*′-dimethyl-*N*,*N*′-bis(2-mercaptoethyl)-1,3-propanediamine}, as functional models for [NiFe]hydrogenases. In acidic media (at pH 4–6), the μ-H ligand of the $Ni^{II}(\mu\text{-}SR)_2(\mu\text{-}H)Ru^{II}$ complexes has H^+ properties, and the complexes catalyse the hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes. A mechanism of the hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes through a low-valent $Ni^{I}(\mu\text{-}SR)_2Ru^{I}$ complex is proposed. In contrast, in neutral–basic media (at pH 7–10), the μ-H ligand of the $Ni^{II}(\mu\text{-}SR)_2(\mu\text{-}H)Ru^{II}$ complexes acts as H^-, and the complexes catalyse the hydrogenation of carbonyl compounds.

Introduction

Hydrogenases (H_2ases) are enzymes that catalyse the reversible interconversion of H_2 into two protons and two electrons under ambient conditions.[1,2] The enzymes also catalyse hydride transfer and electronic reduction of the electron carriers (*e.g.*, NAD^+ and cytochrome c_3) with H_2.[3–10]

H_2ases are classified into two major families on the basis of the metal content of their respective dinuclear active sites, *i.e.*, [NiFe]H_2ases[11–13] and [FeFe]H_2ases.[14,15] X-Ray analysis, spectroscopic techniques and theoretical methods on the structures of the H_2ases have shown that the active sites of both types of H_2ases have characteristic bimetallic units with bis(μ-thiolato) ligands, $M(\mu\text{-}SR')_2M$ {M = Ni or Fe, $(\mu\text{-}SR')_2$ = two bridging cysteine residues, 1,3-propanedithiolato or di(thiomethyl)amine}, and unidentified ligands (depicted as X in Fig. 1).[11–16] The unidentified ligands are proposed to be oxygen ligands such as H_2O, OH^- or O^{2-} in the resting state, and might be a hydride (H^-) ligand in the active state.[11,14–16]

Important parts of our understanding of the H_2-activation mechanism come from studies on protein film voltammetry[17] and the hydrogen isotope exchange reaction between gaseous isotopes (H_2, HD and D_2) and medium isotopes (H^+ and D^+)[18–30] catalysed by H_2ases (eqn (1)), *i.e.*, H_2 bound to the enzyme (E) is split heterolytically to form H^+ and an enzyme hydride (EH^-) (eqn (2)).[18–21] The backward reaction in eqn (2) regenerates H_2. In D_2O, EH^- should react with D^+ to provide E with evolution of HD (eqn (3)). In such a case, H_2 must be initially converted to HD as a single exchange product and then D_2 as a double exchange product in D_2O, *i.e.*, the generation of HD and D_2 must be sequential.[18] However, all experiments of hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes with H_2ases performed till now have shown that the single exchange product (HD) and the double exchange products (D_2 or H_2) were formed simultaneously.[18–30] Thus, the detail of the mechanism of the hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes has so far been the subject of controversy.

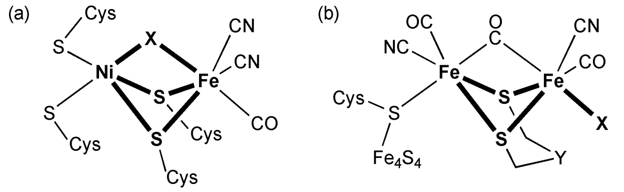

Fig. 1 Active site structures of resting forms of [NiFe]H_2ases (a) and [FeFe]H_2ases (b) (X = H_2O, OH^- or O^{2-}, Y = CH_2 or NH).

$$H_2 + 2D^+ \underset{0<x<1}{\rightleftharpoons} xHD + (1-x)D_2 + xD^+ + (2-x)H^+ \tag{1}$$

$$H_2 + E \rightleftharpoons H^+ + EH^- \tag{2}$$

$$D^+ + EH^- \rightleftharpoons HD + E \tag{3}$$

There are a few studies of the hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes and hydrogenation of unsaturated compounds catalysed by the $M(\mu\text{-}Z)_2M$ (M = metal ions, Z = thiolato, sulfido or hydrosulfido ligands) complexes (Table 1).[31–40] However, time-dependent

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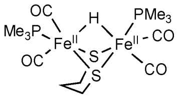
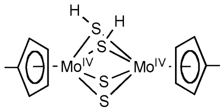
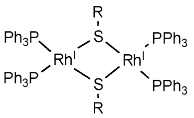
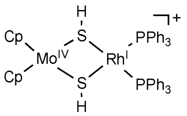
† Electronic supplementary information (ESI) available: Electrospray ionisation mass spectra of **2** (Fig. S1), IR spectra of **2** (Fig. S2), ^1H NMR spectrum of **4** in H_2O (Fig. S3), pH-dependent profile of TOFs for the hydrogenation of glyoxylic acid (Fig. S4) and XPS of **1**, **2** and **3** (Fig. S5). See DOI: 10.1039/b807555g

Table 1 Hydrogen isotope exchange reaction between gaseous isotopes (H_2, HD and D_2) and medium isotopes (H^+ and D^+) and hydrogenation of substrates catalysed by $M(\mu\text{-}Z)_2M$ (M = metal ions, Z = thiolato, sulfido or hydrosulfido ligands) complexes

		Isotope exchange		Hydrogenation	
Entry	Catalyst	System	Time-dependent generation of isotopes	Substrate/product	Solvent
1[a]		H_2/D^+ D_2/H^+	ND[e]	Ethylene/ethane	Dichloromethane
2[b]		H_2/D^+	ND[e]	Sulfur/hydrogen sulfide[f]	Chloroform-d_1
3[c]		—	—	Cyclohexene/cyclohexane	Toluene
4[d]		—	—	1-Octyne/octane, 1-octene and 2-octene	Acetone
5	This work	H_2/D^+ D_2/H^+	Simultaneous	Benzaldehyde/benzyl alcohol	Water

[a] Ref. 32–35. [b] Ref. 36. [c] Ref. 39. [d] Ref. 40. [e] ND: not determined. [f] Hydrogenation of β-bromostyrene and azobenzene was also reported by similar complexes (ref. 37 and 38).

hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes has never been carried out with the $M(\mu\text{-}Z)_2M$ complexes (indicated as ND in Table 1).[41–50] All hydrogenation with the $M(\mu\text{-}Z)_2M$ complexes proceeds in organic solvents but not in water in which the H_2ases operate.

Frontier works on model studies for [NiFe]H_2ases have been carried out by Rauchfuss and co-workers, Artero and Fontecave and co-workers and DuBois and co-workers.[51,52]

We recently reported[53] the synthesis and structures of water-soluble $[Ni^{II}(\mu\text{-}SR)_2Ru^{II}(OH_2)(\eta^6\text{-}C_6Me_6)](OTf)_2$ {[**1**]$(OTf)_2$, $(\mu\text{-}SR)_2$ = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-mercaptoethyl)-1,3-propanediamine, OTf = CF_3SO_3} and $[Ni^{II}(OH_2)(\mu\text{-}SR)_2(\mu\text{-}H)Ru^{II}(\eta^6\text{-}C_6Me_6)](NO_3)$ {[**2**](NO_3)} as functional models for the resting form (E) and the active form (EH^-) of [NiFe]H_2ases, respectively (Fig. 2).[54] The structures of **1** and **2** were determined by X-ray and neutron diffraction analyses.

We report herein the pH-dependent hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes at pH 4–6 catalysed by **2** *via* a low-valent intermediate $[Ni^{I}(\mu\text{-}SR)_2Ru^{I}(\eta^6\text{-}C_6Me_6)]$ (**3**), and hydrogenation of the carbonyl compounds at pH 7–10 catalysed by $[Ni^{II}(OH)(\mu\text{-}SR)_2(\mu\text{-}H)Ru^{II}(\eta^6\text{-}C_6Me_6)]$ (**4**), which is a deprotonated species of **2** whose pK_a value is 6.5 (Fig. 3).

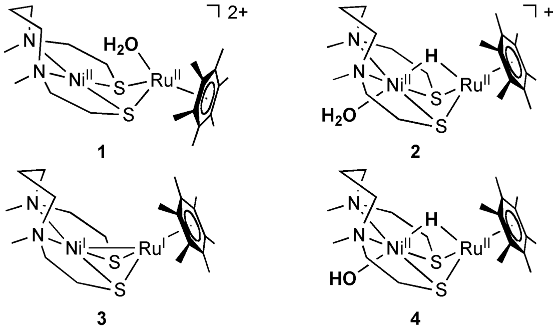


Fig. 2 Water-soluble $Ni(\mu\text{-}SR)_2Ru$ {$(\mu\text{-}SR)_2$ = *N*,*N*′-dimethyl-*N*,*N*′-bis-(2-mercaptoethyl)-1,3-propanediamine} complexes **1**–**4**.

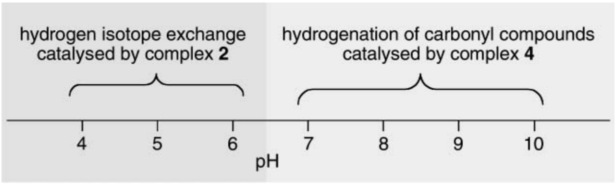


Fig. 3 pH-Dependent hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes and hydrogenation of the carbonyl compounds catalysed by the $Ni(\mu\text{-}H)Ru$ complexes.

Experimental

Materials and methods

$[Ni^{II}(\mu\text{-}SR)_2Ru^{II}(OH_2)(\eta^6\text{-}C_6Me_6)](OTf)_2$ {[**1**]$(OTf)_2$, $(\mu\text{-}SR)_2$ = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-mercaptoethyl)-1,3-propanediamine, OTf = CF_3SO_3} was prepared by the method described in the literature.[53] $[Ni^{II}(OH_2)(\mu\text{-}SR)_2(\mu\text{-}H)Ru^{II}(\eta^6\text{-}C_6Me_6)](NO_3)$

{[**2**](NO_3)} was synthesised from the reaction of **1** with H_2 (0.1 MPa) in the range of pH 4–7 at 25 °C.[53] The manipulations in the acidic media were carried out with plastic- and glassware (without metals). Distilled water, 0.1 M $NaOH/H_2O$ and 0.1 M HNO_3/H_2O were purchased from Wako Pure Chemical Industries, Ltd., 65% DNO_3/D_2O (99% D) was purchased from Isotec Inc., K_2DPO_4 (99% D) was purchased from CDN Isotopes, CH_3COOD (99% D) was purchased from Aldrich Co., and D_2O (99.9% D), 40% $NaOD/D_2O$ (99% D) and KD_2PO_4 (98% D) were 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., D_2 gas (99.5%) was purchased from Sumitomo Seika Chemicals Co., Ltd., and HD gas (HD 97%, H_2 1.8%, D_2 1.2%) was purchased from Isotec Inc.; these were used without further purification.

Matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry (MALDI-TOF-MS) was recorded on ultraflex TOF/TOF (Bruker Daltonics), where dithranol was used as a matrix. Electrospray ionisation mass spectrometry (ESI-MS) data were obtained by an API 365 triple-quadrupole mass spectrometer (PE-Sciex) in the positive detection mode, equipped with an ion spray interface. The sprayer was held at a potential of +5.0 kV, and compressed N_2 was employed to assist liquid nebulisation. ^1H NMR spectra were recorded on a JEOL JNM-AL300 spectrometer at 23 °C. H_2, HD and D_2 gases were determined using Shimadzu GC-14B and GC-8A (He carrier) with a $MnCl_2$–alumina column (model: Shinwa OGO-SP) at −196 °C (liquid N_2) and equipped with a thermal conductivity detector. IR spectra were recorded on a Thermo Nicolet NEXUS 8700 FT-IR instrument from 650 to 4000 cm^{-1} using 2 cm^{-1} standard resolution at ambient temperature. X-Ray photoelectron spectra (XPS) were measured on a VG Scientific ESCALAB MK II electron spectrometer by use of Mg-K_α radiation, and the binding energies were corrected by assuming a C 1s binding energy of the carbon atoms of the ligand in the specimens as 284.5 eV.[55] A magnetic stirrer (model: Nissin SW-R700) was used.

The pH of the solution was adjusted by using 0.1 M HNO_3/H_2O (pH 1–3), 25 mM CH_3COOH/CH_3COONa (pH 4–6), 25 mM Na_2HPO_4/KH_2PO_4 (pH 7–8) and 0.1 M $NaOH/H_2O$ (pH 9–10) solutions. In a pH range of 1.0–11.0, the pH of the solution was determined by a pH meter (model: TOA HM-5A) equipped with a glass electrode (model TOA GS-5015C). pD Values were corrected by adding 0.4 to the observed values (pD = pH meter reading + 0.4).[56,57] In the biphasic media, the pH value of the aqueous phase is adopted.

[$Ni^{II}(OH_2)(\mu\text{-}SR)_2(\mu\text{-}D)Ru^{II}(\eta^6\text{-}C_6Me_6)$]($NO_3$) {[D-labeled 2]($NO_3$)}

The aqua complex [**1**](NO_3)$_2$ (125 mg, 0.2 mmol) was added to a D_2O solution (5 mL) of K_2DPO_4/KD_2PO_4 (25 mM) at pD 5. D_2 (0.1 MPa) was bubbled through the solution at 23 °C to gradually precipitate dark-red crystals of [D-labeled **2**](NO_3). After 3 h of D_2 bubbling, the crystals were isolated by filtration. Further solid [D-labeled **2**](NO_3) was obtained by evaporating the filtrate to *ca.* 1 mL below 30 °C {yield: 80% based on [**1**](NO_3)$_2$}. ESI-MS analysis of the filtrate has shown a prominent signal at *m/z* 544.2 {[D-labeled **2** − H_2O]$^+$; relative intensity (*I*) = 100% in the range of *m/z* 100–2000}. FT-IR (cm^{-1}, as a KBr disk): 1248 (Ni–D–Ru).

[$Ni^I(\mu\text{-}SR)_2Ru^I(\eta^6\text{-}C_6Me_6)$] (3)

Complex [**2**](NO_3) (15.0 mg, 24.1 μmol) was dissolved in H_2O (2.0 mL) at pH 4 (25 mM sodium acetate buffer), and H_2 gas was bubbled through the solution at 23 °C. After 1 h, the solution was evaporated to give a dark red crude oil, which was extracted with chloroform (1 × 3 mL) and the resulting solution was filtered and evaporated under reduced pressure to give a dark red powder of **3** {yield: 81% based on [**2**](NO_3)}. ^1H NMR (in $CDCl_3$, reference to TMS, 23 °C): δ 2.12 (s, 18H, η^6-C_6Me_6), 1.80–3.08 {m, 20H, (μ-SR)$_2$}. Anal. calc. for **3**·CH_3COONa: $C_{23}H_{41}N_2NaNiO_2RuS_2$: C, 44.24; H, 6.62; N, 4.49%. Found: C, 43.92; H, 6.99; N, 4.20%. It was confirmed by ^1H NMR that the sample for the elemental analysis included one equivalent of sodium acetate, which could be derived from the buffer solution of CH_3COOH/CH_3COONa. MALDI-TOF-MS: *m/z* 542.1 ([**3**]$^{\bullet+}$; *I* = 100% in the range of *m/z* 200–1000). FT-IR (cm^{-1}, as a KBr disk): 2957 (aliphatic C–H), 2924 (aliphatic C–H), 2854 (aliphatic C–H), 1720, 1576 (aromatic C=C), 1457 (aromatic C=C), 1263, 1197, 1178, 1150, 1111, 1072, 1017, 969, 872, 862, 833, 776, 749. XPS: 852.7 eV (Ni $2p_{3/2}$ region), 279.4 eV (Ru $3d_{5/2}$ region).

[$Ni^{II}(OH)(\mu\text{-}SR)_2(\mu\text{-}H)Ru^{II}(\eta^6\text{-}C_6Me_6)$] (4)

Complex **4** can be prepared from complex **1** (method A) or complex **2** (method B) as starting materials as follows.

Method A. The aqua complex [**1**](NO_3)$_2$ (125 mg, 0.20 mmol) was added to an H_2O solution (5 mL, pH 9) of $Na_3PO_4·12H_2O$ (95 mg, 0.25 mmol). H_2 was bubbled through the solution at 25 °C to gradually precipitate dark-red solids of **4**. After 3 h, the solids were collected by filtration, and dried *in vacuo*. Further solid **4** was obtained by concentrating the filtrate to *ca.* 1 mL below 30 °C {total yield: 72% based on [**1**](NO_3)$_2$}.

Method B. Complex [**2**](NO_3) (10.0 mg, 16.0 μmol) was added to H_2O and the pH of the resulting solution was adjusted to pH 9 by using 1 mM $NaOH/H_2O$. The solvent was evaporated to precipitate a dark-red powder of **4**. The powder was collected by filtration, and dried *in vacuo* {yield: 72% based on [**2**](NO_3)}. Anal. calc. for **4**·$NaNO_3$: $C_{21}H_{40}N_3NaNiO_4RuS_2$: C, 39.08; H, 6.25; N, 6.51%. Found: C, 39.54; H, 6.68; N, 6.59%. The sample for the elemental analysis was prepared by method B. Na^+ and NO_3^- in the sample could be derived from the $NaOH/H_2O$ solution used for adjusting the pH of the solution and the counteranion of [**2**](NO_3), respectively. The existence of NO_3^- was confirmed by IR measurement, *i.e.*, a characteristic absorption of uncoordinating NO_3^- was observed at 1384 cm^{-1}. ESI-MS (in CH_3CN) *m/z* 543.2 ([**4** − OH]$^+$; *I* = 100% in the range *m/z* 100–2000). FT-IR {cm^{-1}, as a KBr disk}: 3433 (O–H), 1743 (Ni–H–Ru), 1570 (aromatic C=C), 1473 (aromatic C=C), 1465 (aromatic C=C), 1384 (NO_3^-), 1328, 1290, 1262, 1207, 1110, 1097, 1067, 1044, 1025, 972, 951, 803. XPS: 853.9 eV (Ni $2p_{3/2}$ region), 280.5 eV (Ru $3d_{5/2}$ region).

Typical procedure for hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes catalysed by [2](NO_3)

A 3 mL vial was charged with 1.0 μmol of [**2**](NO_3) and a stir bar under H_2, and was capped with a septum. After injecting 1 mL of Ar-bubbled D_2O into the vial, 1 mL of H_2 gas was removed immediately. The vial was stirred (5000 rpm, Nissin magnetic stirrer Model SW-R700) vigorously at 60 °C for 1 h. The gas present in the vial was sampled using a gas-tight syringe and analysed for H_2, HD and D_2 gases by GC. Isotope ratios for each of the identical runs were averaged. It was confirmed that no isotope exchange reactions between gaseous isotopes and medium isotopes occurred in the absence of **1**, **2** or **3** (as blank experiments). When the experiments were performed using D_2 and H_2O, the results were the same except for the isotope effects, and the H_2/HD ratio was comparable to the D_2/HD ratio of the H_2/D^+ isotope exchange reaction.

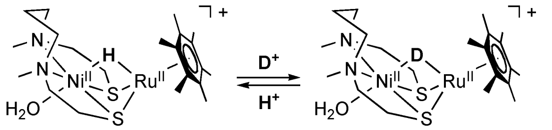
Typical procedure for the hydrogenation of carbonyl compounds catalysed by 4

Benzaldehyde (250 μmol) and **4** (3.1 mg, 5.0 μmol) were dissolved in H_2O (2 mL) at pH 7–10. The solution was stirred under H_2 at a pressure of 0.1–0.7 MPa at 60 °C. After 1 h, the solution was cooled to 0 °C, and the resulting mixture was extracted by $CDCl_3$. The yield of benzyl alcohol in the $CDCl_3$ solution was determined by ^1H NMR with 1,4-dioxane as an internal standard. It was confirmed that no hydrogenation occurred in the absence of **1** or **4** (as blank experiments).

Results and discussion

Behavior of Ni(μ-H)Ru complexes in acidic media (at pH 4–6)

Only crystals of **2** {Ni(μ-H)Ru} and the D-labeled **2** {Ni(μ-D)Ru} available for X-ray analysis were used for all experiments in this study. It is very important to note that the hydride complex **2** does not react with H^+ to evolve H_2 in acidic media at pH 4–6,[58] *i.e.*, complex **2** does not decompose to the aqua complex **1** with the evolution of H_2 in acidic media at pH 4–6. It was confirmed by ESI-MS (Fig. S1 in ESI†) and IR (Fig. S2 in ESI†) that the structure of **2** was preserved in acidic media at pH 4–6. The hydrido ligand of **2** exhibits a protic character and undergoes an H^+/D^+ exchange with D^+ in D_2O at pD 4–6 (eqn (4)).



2 D-labeled **2** (4)

Fig. 4 shows the result of pD-dependent H^+/D^+ exchange for 15 min at 60 °C determined by ESI-MS, which indicates a maximum around pD 4. At pD 4–6, the lower pD of the solution, the faster is the rate of the H^+/D^+ exchange, *i.e.*, the rate of the H^+/D^+ exchange is dependent on D^+ concentration.

A low-valent complex Ni^I(μ-SR)$_2$Ru^I

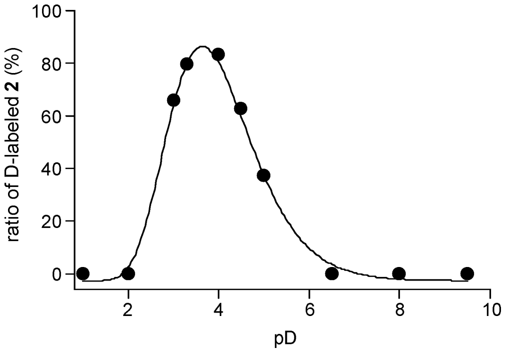


Fig. 4 pD-Dependent H^+/D^+ exchange of the hydrido ligand of [**2**](NO_3) (1.0 μmol) in D_2O (1 mL) at pD 1–10 at 60 °C for 15 min.

Complex [**2**](NO_3) was dissolved in H_2O at pH 4–6. H_2 gas was bubbled through the solution at 23 °C, to evaporate the solvent, for 1 h. The remaining red oil was extracted with chloroform and the resulting solution was filtered and evaporated under vacuum to yield a dark red powder of **3**. It is important to note that the low-valent complex **3** was not obtained from the reaction of **2** with H_2 in neutral–basic media at pH 7–10. Fig. 5a shows a MALDI-TOF mass spectrum of a signal at m/z 542.1 {relative intensity (I) = 100% in the range of m/z 200–1000}. The envelope at m/z 542.1 has a characteristic distribution of isotopomers that matches well with the calculated isotopic distribution for $[\mathbf{3}]^{\bullet+}$ (Fig. 5b and 5c). X-Ray photoelectron spectra (XPS) of **3** show that the binding energies of Ni $2p_{3/2}$ and Ru $3d_{5/2}$ are 852.7 eV and 279.4 eV, which correspond to Ni(I) and Ru(I), respectively (Fig. 6).[59] The values of the binding energies of Ni $2p_{3/2}$ and Ru $3d_{5/2}$ in **3** are lower than those of [**1**]$(NO_3)_2$ (Ni $2p_{3/2}$: 853.9 eV, Ru $3d_{5/2}$: 280.3 eV). ^1H NMR measurement indicates diamagnetism in **3**, *i.e.*, the signals of the

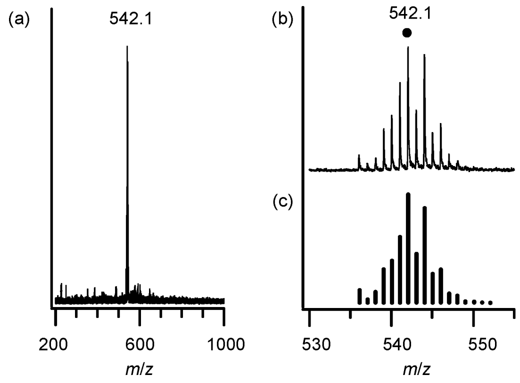


Fig. 5 (a) MALDI-TOF mass spectrum of **3**. Dithranol was used as a matrix. The signal at m/z 542.1 corresponds to $[\mathbf{3}]^{\bullet+}$. (b) The signal at m/z 542.1. (c) Calculated isotopic distribution for $[\mathbf{3}]^{\bullet+}$.

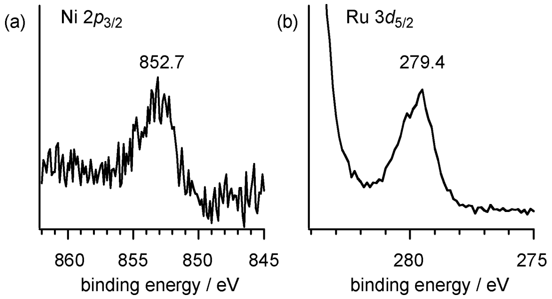


Fig. 6 (a) XPS of Ni 2p region for **3**. (b) XPS of Ru 3d region for **3**.

protons of η^6-C_6Me_6 and $(\mu\text{-}SR)_2$ of **3** were observed at 2.12 and 1.80–3.08 ppm, respectively. The reason for diamagnetism should be explained on the basis of electronic coupling between the two metal ions (Ni^I and Ru^I).

Hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes catalysed by the D-labeled 2 in acidic media (at pH 4–6)

The D-labeled **2** catalyses a pD-dependent hydrogen isotope exchange reaction between H_2 and D_2O as shown in Fig. 7. The pD-dependence of the hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes (Fig. 7) is similar to the pD-dependence in the H^+/D^+ exchange (Fig. 4). The evolution of HD and D_2 was determined by GC.

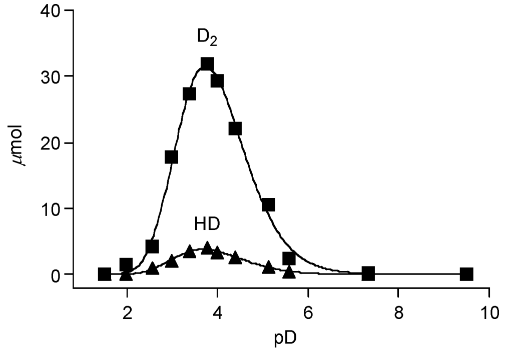


Fig. 7 pD-Dependent generation of HD and D_2 in the reaction of [**2**](NO_3) (1.0 μmol) with H_2 (2.0 cm^3, 84 μmol, 0.1 MPa) in D_2O (1 mL) at 60 °C for 1 h.

The time course of the hydrogen isotope exchange reaction between H_2 and D_2O (or between D_2 and H_2O) catalysed by the D-labeled **2** (or **2**) shows that HD and D_2 (or HD and H_2) are formed simultaneously as shown in Fig. 8a (or Fig. 8b), which agrees with the time-dependent profile in the hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes by H_2ases.[18–30] The data of the consumption of H_2 (Fig. 8a) and D_2 (Fig. 8b) were used for the first-order kinetic plots in Fig. 8c. The consumption of H_2 (or D_2) obeyed the first-order kinetics over 3–5 half-lives. In this case, a kinetic isotope effect {KIE = 1.7, $k_{obs}(H) = 1.03 \times 10^{-4}\ s^{-1}$ and $k_{obs}(D) = 6.11 \times 10^{-5}\ s^{-1}$} was observed (Fig. 8c). The presence of the KIE is consistent with a mechanism in which the rate-determining step involves H–H (or D–D) bond cleavage.

The pH-dependence and time course of the hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes catalysed by **1** and **2** are similar to those catalysed by the D-labeled **2**.

Mechanism of the hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes in acidic media

Based on the results obtained, we propose a mechanism of the hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes. In Fig. 9, D-labeled **2** is used as a starting complex whose μ-D ligand has a D^+ character, but not a D^- character at pD 4–6 (*vide supra*). First, the reaction of the D-labeled **2** with H_2 may produce a single D-labeled dihydride species **Q** (HD hydride) *via* heterolytic activation of H_2. This may be a rate-determining step for the hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes judging from the observed KIE as shown in Fig. 8c. The H^+/D^+ exchange of **Q** with D^+ in D_2O occurs quickly to give a double D-labeled dihydride species **R** (DD hydride). Then, intramolecular reductive elimination of HD from **Q** and D_2 from **R** occurs to give the low-valent complex **3**. This is the reason why HD and D_2 are produced simultaneously (but not sequentially). To complete the catalytic cycle, the D-labeled **2** is regenerated by deuteration of **3**. This is totally different from the previously proposed mechanism of the hydrogen isotope exchange reactions between gaseous isotopes (H_2) and medium isotopes (D_2O), where the hydrido ligand of the metal hydride species (M–H) acts as H^- and reacts with medium D^+ to form HD as the first step in the reaction.[43,47,49] It was confirmed that the low-valent complex **3** also catalysed the hydrogen isotope exchange reaction between H_2 and D_2O (or between D_2 and H_2O).

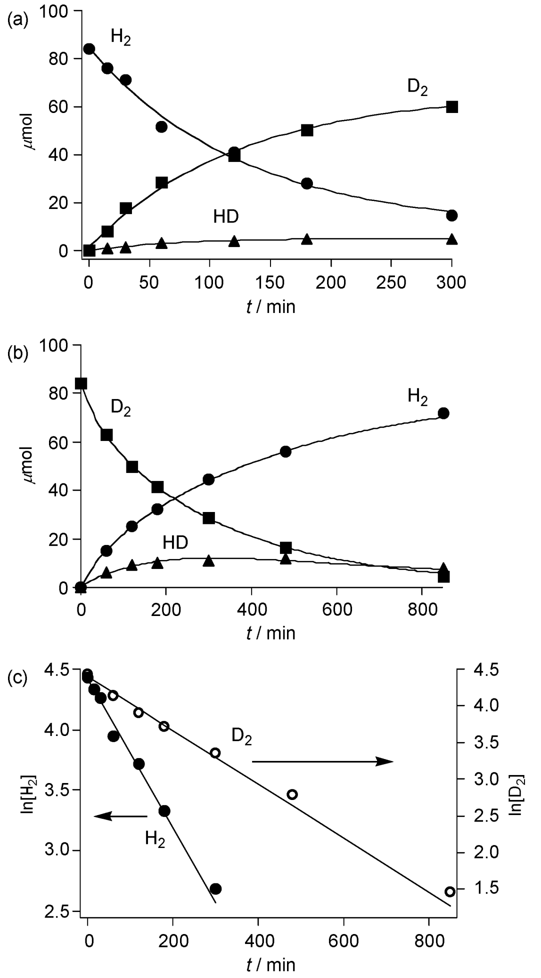


Fig. 8 (a) Time course of the generation of HD and D_2 and the consumption of H_2 determined by GC analysis in the reaction of [D-labeled **2**](NO_3) (1.0 μmol) with H_2 (2.0 cm^3, 84 μmol, 0.1 MPa) in D_2O (1 mL, pD 4.0) at 60 °C. (b) Time course of the generation of HD and H_2 and the consumption of D_2 determined by GC analysis in the reaction of [**2**](NO_3) (1.0 μmol) with D_2 (2.0 cm^3, 84 μmol, 0.1 MPa) in H_2O (1 mL, pH 4.0) at 60 °C. (c) The first-order kinetic plots for the consumption of H_2 (Fig. 8a) and D_2 (Fig. 8b).

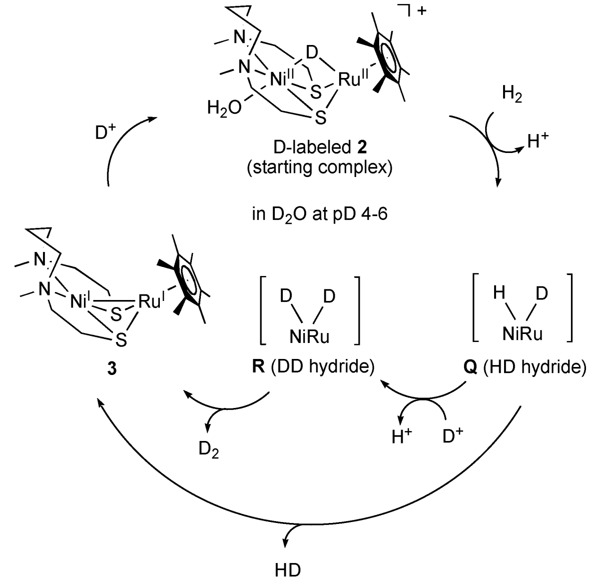
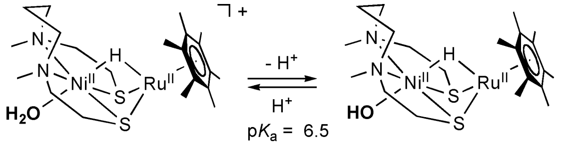


Fig. 9 A proposed mechanism of the hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes. D-Labeled **2** is used as a starting complex with H_2 in D_2O at pD 4–6.

Behavior of Ni(μ-H)Ru complexes in neutral-basic media (at pH 7–10)

Complex **2** is reversibly deprotonated to form **4**, which is a deprotonated species of **2**, in neutral–basic media at pH 7–10 (eqn (5)).[60]

 (5)

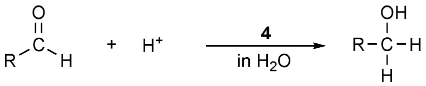
2
(stable at pH 4-6)

4
(stable at pH 7-10)

UV-vis titration experiments revealed that the pK_a value of **2** was 6.5 (Fig. 10). It is well known that aqua complexes can deprotonate to form hydroxo complexes in neutral–basic media.[61–65] ^{1}H NMR measurements indicate paramagnetism in **4** (Fig. S3 in ESI†). A similar character was observed in **2**.[53] In an IR spectrum of **4** in the 650–4000 cm^{-1} region as a KBr disk, a peak at 3433 cm^{-1} was assigned to ν(O–H) that shifts to 2688 cm^{-1} by isotopic substitution of a hydrogen atom in the hydroxo ligand (OD),[66] although the O–H stretching observed by IR is not direct evidence for the existence of **4**.[67]

Stoichiometric hydrogenation of carbonyl compounds with 4 in neutral-basic media at pH 7–10 (without H_2)

Complex **4** has a reducing ability toward carbonyl compounds such as benzaldehyde at pH 7–10 under stoichiometric conditions (**4** : carbonyl compound = 1 : 1) in the absence of H_2 (eqn (6)),

 (6)

$$\underset{\mathrm{R}}{}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\underset{\mathrm{H}}{} + H^+ \xrightarrow[\text{in } H_2O]{\mathbf{4}} \mathrm{R{-}}\overset{\overset{\mathrm{OH}}{|}}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}\mathrm{{-}H} \quad (6)$$

e.g., benzaldehyde is reduced to benzyl alcohol (yield: 6%) with **4** at pH 8 at 60 °C for 1 h.

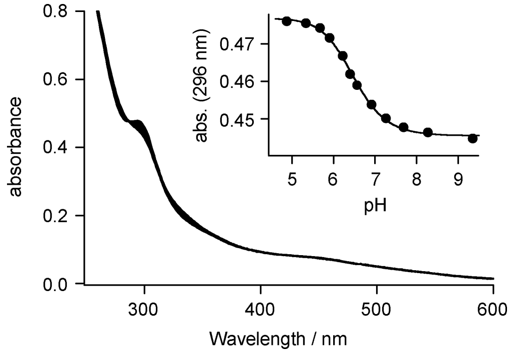


Fig. 10 pH-Dependent UV-vis spectra of **2** (4.7×10^{-5} M) in the pH range 4.5–9.5. The inset gives a plot of absorbance (l = 296 nm) *versus* pH. Experiments were performed by the titration of **2** with 0.1 M NaOH/H_2O at 23 °C.

Fig. 11 shows the pH-dependent yield (based on **4**) of the *o*-fluorobenzyl alcohol that was obtained by a reaction of **4** with *o*-fluorobenzaldehyde under N_2 in the absence of H_2 at 60 °C for 15 min, *i.e.*, the reduction takes place in the neutral–basic media at pH 7–10.

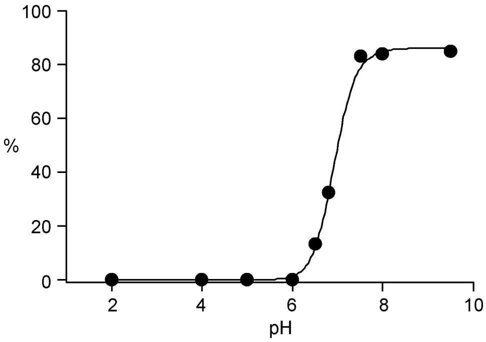
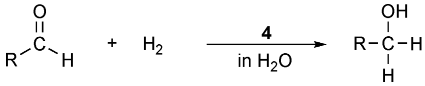


Fig. 11 pH-Dependent yield (based on **4**) of *o*-fluorobenzyl alcohol from the reaction of *o*-fluorobenzaldehyde (500 μmol) with **4** (5 μmol) in H_2O (2 mL) at 60 °C for 15 min under N_2 in the absence of H_2.

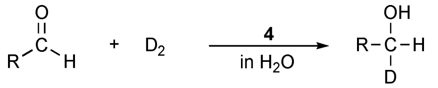
Catalytic hydrogenation of carbonyl compounds with 4 in neutral–basic media at pH 7–10 (with H_2)

On the other hand, under catalytic conditions (0.5 MPa of H_2), benzaldehyde (50 equivalents) is reduced to benzyl alcohol catalysed by **4** in H_2O at pH 8 at 60 °C for 12 h (yield: 98%, eqn (7)).

 (7)

$$\underset{\mathrm{R}}{}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\underset{\mathrm{H}}{} + H_2 \xrightarrow[\text{in } H_2O]{\mathbf{4}} \mathrm{R{-}}\overset{\overset{\mathrm{OH}}{|}}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}\mathrm{{-}H} \quad (7)$$

To the best of our knowledge, this is the first example of the hydrogenation of substrates catalysed by M(μ-Z)$_2$M (M = metal ions, Z = thiolato, sulfido or hydrosulfido ligands) complexes in aqueous media.[54] ^{1}H NMR experiments revealed that the D-labeled hydrogen atoms were incorporated into the carbonyl compounds when D_2 was used as the hydrogen donor in the hydrogenation (eqn (8)).



$$R{-}C(=O){-}H + D_2 \xrightarrow[\text{in } H_2O]{4} R{-}CH(OH){-}D \qquad (8)$$

The pH-dependence on the catalytic reduction of glyoxylic acid under H_2 (0.5 MPa) is similar to the pH-dependence on the reduction under the stoichiometric conditions described above (Fig. S4 in ESI†).

Fig. 12 reveals temperature-dependent turnover frequencies {TOFs = (mol of product formed/mol of catalyst) per h} in the hydrogenation of *o*-fluorobenzaldehyde catalysed by **4** in H_2O at pH 8 at 0.5 MPa of H_2. The TOFs of the hydrogenation were drastically increased above 40 °C. The catalytic reactions were carried out at 60 °C, and it was confirmed by ESI-MS that complex **4** was quite stable at 60 °C under Ar at pH 7–10 in the absence of reducible aldehydes. Fig. 13 shows the dependence of TOFs upon concentrations of *o*-fluorobenzaldehyde used in the hydrogenation catalysed by **4** in H_2O at pH 8 at 60 °C. The TOFs of the hydrogenation of aldehydes examined in this study saturate at a 1 : 50 ratio of **4** : aldehydes. As shown in Fig. 14, the TOFs of the hydrogenation of *o*-fluorobenzaldehyde catalysed by **4** in H_2O at pH 8 at 60 °C are dependent on the pressure of H_2 in the range from 0.1 to 0.5 MPa, and saturate at 0.5 MPa. Fig. 15 shows the time course of the turnover numbers (= TONs, mol of product formed/mol of catalyst) in the hydrogenation of *o*-fluorobenzaldehyde under the optimised catalytic conditions (pH 8, 60 °C, 0.5 MPa of H_2, 1 : 50 ratio of **4** : aldehydes). In addition, it was confirmed that the catalyst **4** could be reused at least three times; *i.e.*, upon addition of more substrates after the reaction, the catalytic cycle was resumed (Fig. 16), though the catalyst **4** was gradually deactivated.

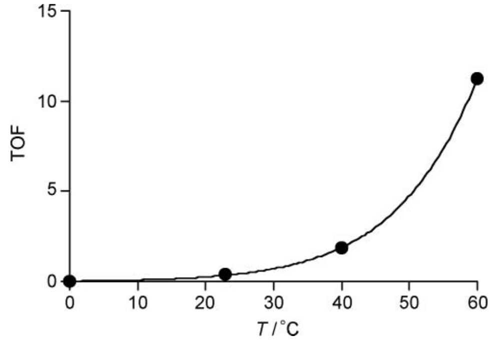


Fig. 12 Temperature-dependent profile of TOFs {(mol of product formed/mol of catalyst) per h} of the hydrogenation of *o*-fluorobenzaldehyde (250 µmol) with **4** (5 µmol) in H_2O (2 mL) at pH 8 at 0.5 MPa of H_2.

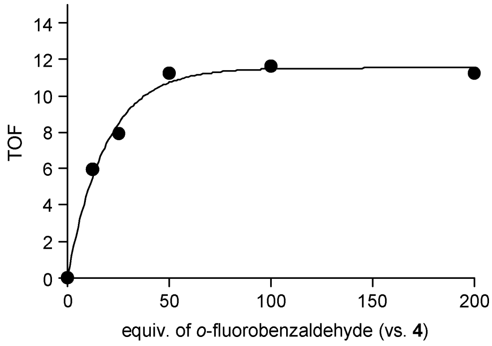


Fig. 13 TOFs {(mol of product formed/mol of catalyst) per h} depending upon the number of moles of substrates for the hydrogenation of *o*-fluorobenzaldehyde with **4** (5 µmol) in H_2O (2 mL) at pH 8 at 60 °C at 0.5 MPa of H_2.

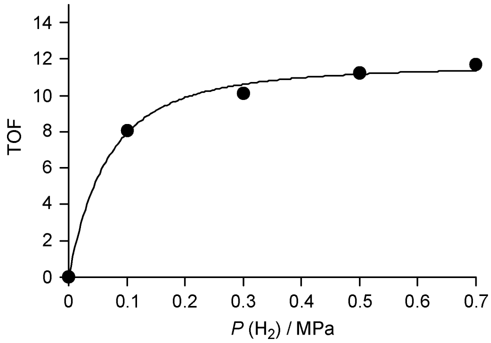


Fig. 14 H_2 Pressure-dependent TOFs {(mol of product formed/mol of catalyst) per h} for the hydrogenation of *o*-fluorobenzaldehyde (250 µmol) with **4** (5 µmol) in H_2O (2 mL) at pH 8 at 60 °C.

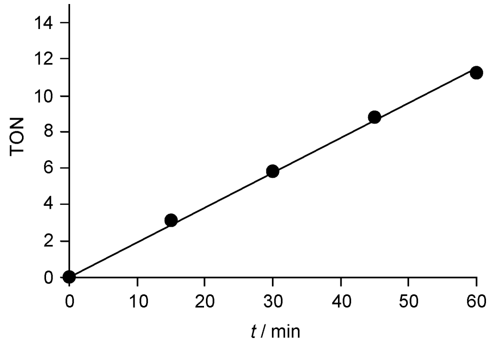


Fig. 15 Time course of the TONs of the hydrogenation of *o*-fluorobenzaldehyde (250 µmol) with **4** (5 µmol) in H_2O (2 mL) at 60 °C at 0.5 MPa of H_2.

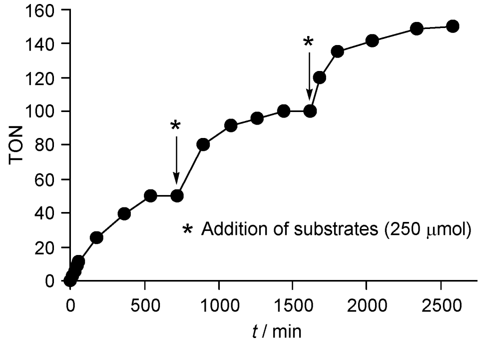
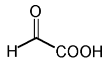
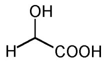
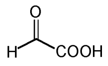
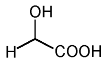
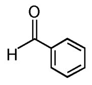
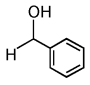
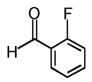
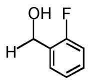


Fig. 16 Resumption of the catalytic hydrogenation of *o*-fluorobenzaldehyde (250 µmol) with **4** (5 µmol) in H_2O (2 mL) at 60 °C at 0.5 MPa of H_2.

Table 2 summarises the hydrogenation of aldehydes catalysed by **4** under the optimised catalytic conditions. The water-soluble aldehyde (glyoxylic acid) is converted to the corresponding alcohol much more efficiently than water-insoluble aldehydes (benzaldehyde and *o*-fluorobenzaldehyde). The TOF of the hydrogenation of a benzaldehyde derivative containing an electron-withdrawing

Table 2 Hydrogenation of water-soluble aldehydes (entries 1 and 2) in water and water-insoluble aldehydes (entries 3 and 4) in biphasic media catalysed by **4** at pH 8[a]

Entry	Substrate	Product	TOF[b]	t/h	Yield (%)	T/°C
1			3	24	44	23
2			24	4	98	60
3			6	12	98	60
4			11	9	99	60

[a] In the case of biphasic media (entries 3 and 4), the pH value of the aqueous phase is adopted. [b] Turnover frequency: (mol of product formed/mol of **4**) per h.

group (*o*-fluorobenzaldehyde) is higher than the TOF of the hydrogenation of benzaldehyde at pH 8 at 60 °C.

Mechanism of the catalytic hydrogenation of carbonyl compounds

The catalytic cycle of the hydrogenation of the water-soluble and water-insoluble aldehydes catalysed by **4** is shown in Fig. 17. The hydride complex **4** reacts with aldehydes to afford the corresponding alcohols and the aqua complex **1**. Complex **4** is regenerated by the reaction of the aqua complex **1** with H_2 at pH 7–10. It is known that the H_2O ligand accelerates the heterolytic H_2-activation in polar solvents to release H_3O^+.[68–70]

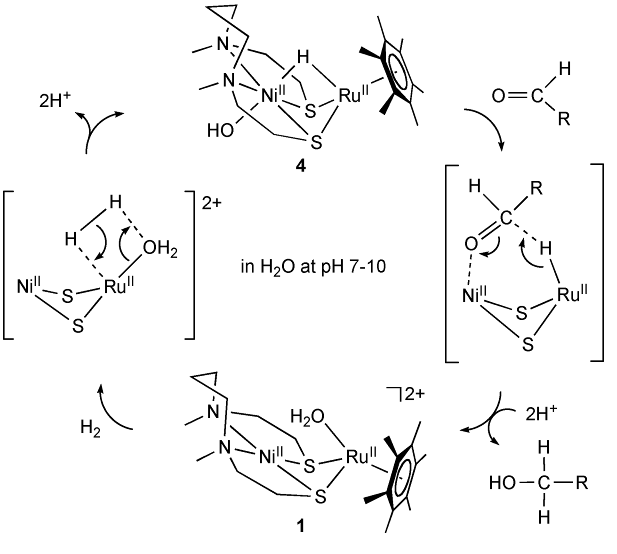


Fig. 17 A proposed mechanism of the hydrogenation of the carbonyl compounds in H_2O at pH 7–10.

Conclusions

We have succeeded in the pH-dependent hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes catalysed by **2** at pH 4–6 and hydrogenation of carbonyl compounds catalysed by **4** at pH 7–10. In the hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes, the generation of HD and D_2 (or HD and H_2) is simultaneous and pH-dependent, which is similar to H_2ases. A low-valent $Ni^I(\mu\text{-}SR)_2Ru^I$ complex **3** has been isolated by the reaction of **2** with H_2 in acidic media at pH 4–6. The formation of **3** by reductive elimination of HD and D_2 (or HD and H_2) from the dihydride species produced by the reaction of **2** with H_2 (or D_2) is the key step for the simultaneous generation of HD and D_2 (or HD and H_2). In the hydrogenation, complex **4** can reduce the aldehydes to the corresponding alcohols in H_2O. Thus, the μ-H ligand of the $Ni^{II}(\mu\text{-}SR)_2(\mu\text{-}H)Ru^{II}$ complexes has both protic character (at pH 4–6) and hydridic character (at pH 7–10) depending on pH.

Acknowledgements

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