nature chemistry

ARTICLES

PUBLISHED ONLINE: 10 MARCH 2013 | DOI: 10.1038/NCHEM.1595

A homogeneous transition metal complex for clean hydrogen production from methanol–water mixtures

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The development of an efficient catalytic process that mimics the enzymatic function of alcohol dehydrogenase is critical for using biomass alcohols for both the production of H_2 as a chemical energy carrier and fine chemicals under waste-free conditions. Dehydrogenation of alcohol–water mixtures into their corresponding acids with molecular hydrogen as the sole by-product from the reaction can be catalysed by a ruthenium complex with a chelating bis(olefin) diazadiene ligand. This complex, $[K(dme)_2][Ru(H)(trop_2dad)]$, stores up to two equivalents of hydrogen intramolecularly, and catalyses the production of H_2 from alcohols in the presence of water and a base under homogeneous conditions. The conversion of a $MeOH–H_2O$ mixture proceeds selectively to CO_2/H_2 gas formation under neutral conditions, thereby allowing the use of the entire hydrogen content (12% by weight). Isolation and characterization of the ruthenium complexes from these reactions suggested a mechanistic scenario in which the $trop_2dad$ ligand behaves as a chemically 'non-innocent' co-operative ligand.

Methanol or simple alcohols are harmless, easy to store, water-soluble fuels that can be produced industrially, on a large scale, from renewable resources. The conversion of methanol–water mixtures into CO_2 and H_2 gases (known as methanol steam reforming) is widely applied in on-board power generation using indirect methanol fuel cells, and has reached an advanced stage of development. The reaction typically proceeds using heterogeneous catalysts under high pressure and in a temperature range of 200–300 °C. Under these conditions, carbon monoxide (CO) can contaminate the product gas, and may poison the fuel cell catalysts. The development of catalytic systems that operate at lower temperatures and produce pure hydrogen is desirable[1], and approaches based on heterogeneous photocatalytic conversions have been reported recently[2,3]. Homogeneous catalysts for the production of hydrogen from methanol have been investigated for decades, but they show little activity and selectivity[4]. Indeed, some carbon-containing by-products were obtained, including mixtures of formaldehyde[5], methyl formate[6], formate salts[7], acetic acid[8] or dimethyl acetal[9], significantly lowering the efficiency of the process[10].

In their pioneering work, Shvo and colleagues[11] demonstrated that simple alcohols can be converted into esters and hydrogen, and established the possible strategic role of a chemically non-innocent co-operative ligand in the coordination sphere of a metal catalyst. Recently, Milstein *et al.* and others have developed this concept further, and have synthesized ruthenium complexes with co-operative pincer-type ligands (Fig. 1) as efficient catalysts for the dehydrogenation of alcohols according to $R–CH_2–OH + XH \rightarrow RCOX + 2\ H_2$; $X = OR', NHR'$ (refs 12–14).These slightly endothermic reactions proceed with the removal of molecular hydrogen at temperatures above 70 °C[15,16]. Under mild conditions, and in the presence of water and a hydrogen acceptor, rhodium(I) amido complexes efficiently catalyse the conversion of primary alcohols, polyols and sugars to carboxylates as products[17,18]. The amido group serves as a co-operative ligand, and hydrogen can be added reversibly across the Rh–N bond. Because of their thermal instability, these rhodium complexes do not allow efficient catalysis under acceptor-less conditions, but they may be used as molecular electrocatalysts on a carbon conductive support in an organometallic fuel cell[19]. In this device, ethanol and water are converted into acetate and electric current with a very high efficiency per metal atom[20].

Important advances have been made in the recycling of CO_2 into methanol[21] in efforts to decrease the use of syn-gas derived from hydrocarbons[22]. However, the development of a homogeneous single-site catalyst for the selective conversion of 1:1 methanol–water mixtures into CO_2 and H_2 (or electric current), which would make use of the full gravimetric content of the hydrogen (12 wt%) of the system, has not been reported to date. Here, we report the synthesis of a homogeneous catalyst that promotes the coupling of

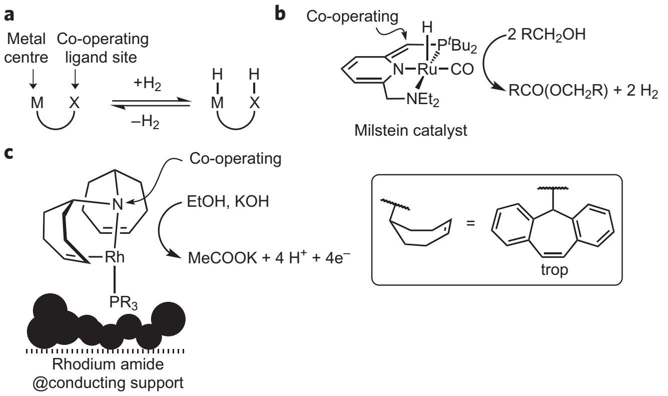

Figure 1 | Metal–ligand co-operativity for hydrogen splitting and evolution. **a**, The H_2 molecule is cleaved in a heterolytic reaction leading to M–H and X–H (M = metal centre; X = chemically non-innocent co-operative ligand site). **b**, Milstein's Ru(II) catalyst contains a co-operative dearomatized pincer ligand and converts alcohols to esters under liberation of H_2. **c**, A rhodium(I) complex with a co-operative amido ligand serves as molecular electrocatalyst for the conversion of alkaline solutions of alcohols into carboxylates, protons and electric current.

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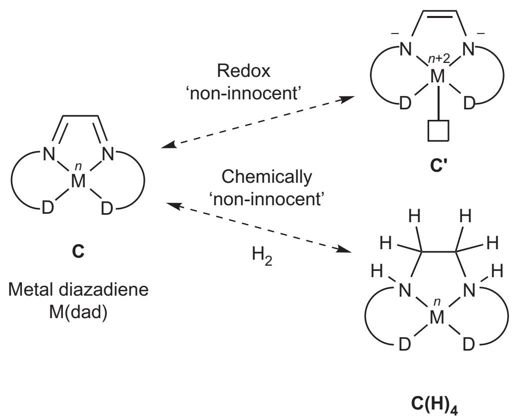

Figure 2 | Redox-active or chemically active metal–diazadiene–olefin combination. Isomer **C** carries a neutral dad ligand, whereas in **C′** the ligand has been reduced to a bis(anionic) bis(amido)enediamide ligand and the oxidation state of the metal increased by two units. A free coordination site at the metal centre is obtained (indicated by a square in **C′**) without significant structural changes to the complex. Furthermore, a polar metal amide bond is generated that allows the addition of polar substrates (hydroxy compounds) or the heterolytic splitting or release of hydrogen, leading to **C(H)$_4$**. D = neutral two-electron donor site.

methanol and water into formic acid and 2 equiv. of hydrogen (equation (1)) followed by a further conversion of the formic acid into CO_2 as well as a further 1 equiv. of dihydrogen (equation (2)):

$$H_3COH + H_2O \rightarrow HCOOH + 2H_2 \quad \Delta H_r = 53.3\,\mathrm{kJ\,mol^{-1}} \quad (1)$$

$$HCOOH \rightarrow CO_2 + H_2 \quad \Delta H_r = -14.5\,\mathrm{kJ\,mol^{-1}} \quad (2)$$

The first step in this sequence is endothermic, and the second is exothermic, making the whole process mildly endothermic by $\Delta H_r = 38.8$ kJ mol^{-1} (www.nist.gov/index.html). This rational approach is based on mechanistic insights on alcohol dehydrogenation reactions and excludes the formation of poisonous CO. Moreover, the second step, based in the decomposition of formic acid into CO_2 and H_2, has been investigated extensively using homogeneous and heterogeneous catalysts[23–25].

Results and discussion

We focused on the synthesis of metal complexes bearing the 1,4-bis(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)-1,4-diazabuta-1,3-diene ligand (trop$_2$dad; see top of Fig. 3a), taking into account the following considerations. (i) Metal complexes with a 1,4-diazadiene ligand (dad) are classical examples of complexes with redox 'non-innocent' ligands and can act as electron reservoirs. This non-innocent behaviour of diimine-type ligands has been studied extensively[26–29]. The chosen metal–ligand combination can be described by structures **C** and **C′** in Fig. 2 (either resonance forms or distinctive electronic states)[30,31]. (ii) These diazadiene ligands also behave as chemically 'non-innocent' ligands[32–35], and have an intrinsic reactivity towards 'storing' several equivalents of hydrogen, as indicated in **C(H)$_4$** (Fig. 2). (iii) Olefins are a further recently recognized class of 'non-innocent' ligands[36]. Their electronic flexibility accommodates the metal centres, especially in low-valence configurations, and they have proven to be potent steering ligands in catalysis[37]. We deemed the olefinic group of the 5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl (trop) residue to act as an additional donor site (D) for the construction of a robust tetrachelating template ligand.

The synthesis of trop$_2$dad was straightforward, as was coordination onto rhodium and iridium (+1) centres[38]. In contrast, the synthesis of Ru(trop$_2$dad)-type complexes proved more difficult and required a two-step reaction. The reaction between the more flexible ligand trop$_2$dae **1** [*N*,*N′*-bis(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)-1,4-diaminoethane] and [$RuCl_2(PPh_3)_3$] cleanly gave the ruthenium precursor complex **2** (Fig. 3a). The ruthenium hydride derivative [K(dme)$_2$][RuH(trop$_2$dad)] **3** was isolated in high yield (81%) from the reaction of complex **2** with 3 equiv. of KO^{t}Bu under an atmosphere of hydrogen (1.5 bar). Formation of the enediamide ligand and the presence of the hydride in complex **3** are readily recognized by the characteristic chemical shift in the ^{1}H NMR spectrum assigned to the enaminic protons of the trop-N-*CH*=*CH*-N-trop (δ ^{1}H = 6.64 ppm) as well as a sharp resonance centred at –10.25 ppm corresponding to the hydride ligand.

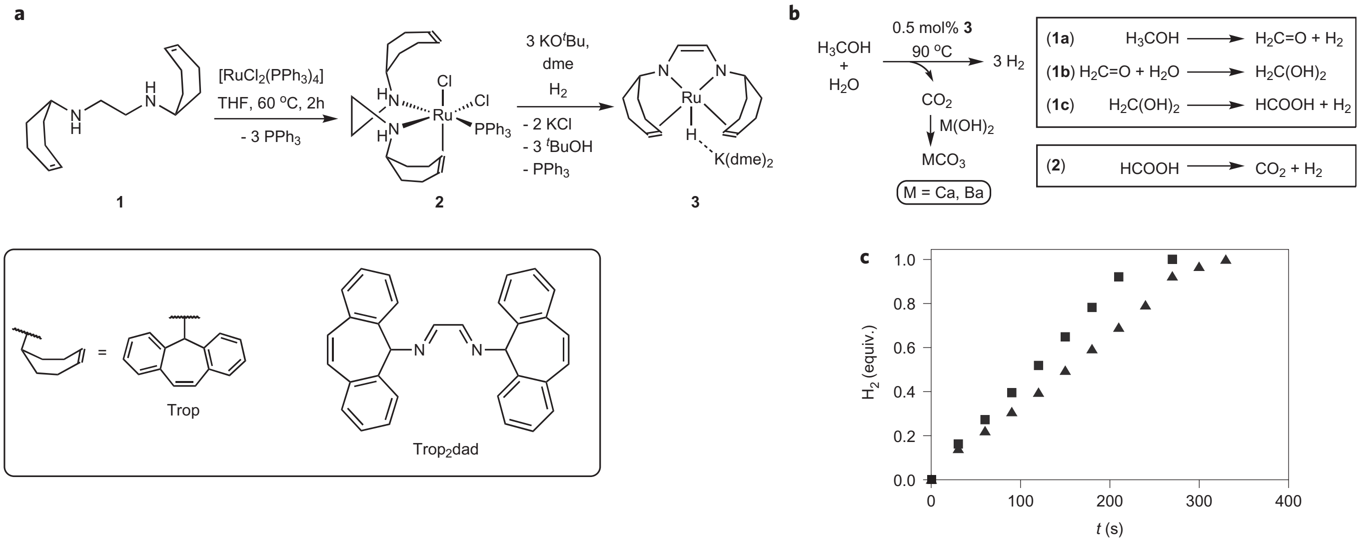

Figure 3 | Preparation and reactivity of [K(dme)$_2$][Ru(H)(trop$_2$dad)]. a, Illustration of the trop$_2$dad ligand, simplified drawing of the 1,4-bis(5*H*-dibenzo[*a,d*]cyclohepten-5-yl = trop moiety used throughout this Article, and two-step synthesis of K[Ru(II)(H)(tropdad)] **3** via complex **2** from accessible precursors. **b**, Conversion of a 1:1 MeOH/H_2O mixture to H_2/CO_2 catalysed by complex **3.** Reaction equations (**1a**), (**1b**), (**1c**) and (**2**) show proposed reaction steps. **c**, Plot of hydrogen formation versus time from formic acid decomposition (equation (2)). Reactions were carried out with pure formic acid (1 M, 1 mmol) in dioxane solution (black filled triangles) or formic acid (1 M, 1 mmol)/triethylamine (5:2 molar ratio) in dioxane solution (black filled squares).

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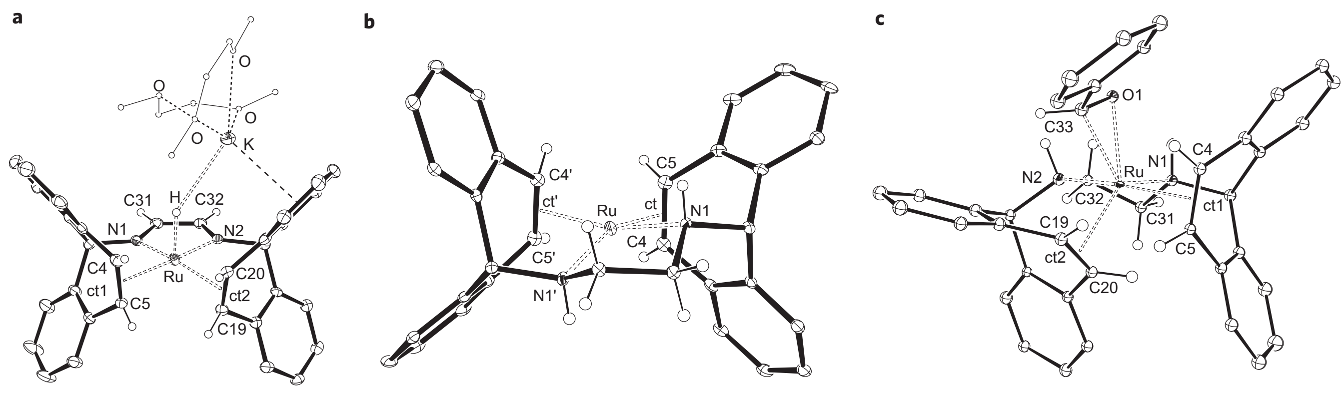

Figure 4 | X-ray crystal structures (ORTEP) of catalyst 3 and key intermediates 5 and 6. Thermal ellipsoids are drawn at 30% probability level (except for **6** which was not refined anisotropically). Non-relevant hydrogen atoms have been removed for clarity. ct is the centroid of the coordinated C4=C5 and C19=C20 bonds, respectively. Selected bond distances (Å) and angles (deg). **a**, $[K(dme)_2][RuH(trop_2dad)]$ (**3**): Ru-N1 1.963(4), Ru-N2 1.978(4), Ru-H 1.60(6), C4-C5 1.440(7), C19-C20 1.434(6), Ru-ct1 2.034(5), Ru-ct2 2.033(5), N1-C31 1.356(6), N2-C32 1.348(6), C31-C32 1.377(7); N1-Ru-H 98(2), ct1-Ru-H 94(2), N1-Ru-N2 79.0(2), N1-Ru-ct2 161.0(2). **b**, $[Ru(0)(trop_2dae)]$ (**5**): Ru-N1/1′ 2.121(2), C4/4′ = C5/5′ 1.453(3), Ru-ct1/1′ 1.970(2), N1/1′-C16/16′ 1.487(3), N1/1′-Ru-ct1/1′ 92.2(1). **c**, $[Ru(0)(OCHPh)(trop_2dae)]$ (**6**): Ru-N1 2.173(6), Ru-N2 2.159(6), Ru-C33 2.138(8), Ru-O1 2.120(5), Ru-ct1 2.077(7), C4-C5 1.416(1), C19-C20 1.450(1), N1-C31 1.48(1), N2-C32 1.51(1), C31-C32 1.53(1), O1-C33 1.310(9); N1-Ru-C33 122.4(3), N1-Ru-O1 86.6(2), N1-Ru-N2 80.7(2), N1-Ru-ct1 87.9(3).

An X-ray diffraction study of a deep-purple oxygen-sensitive single crystal of **3** determined its structural features (Fig. 4a). The $[Ru(H)(trop_2dad)]^-$ anion and the $[K(dme)_2]^+$ cation form an electrostatically enforced host–guest complex in which the K^+ ion interacts with one of the benzo groups of the $trop_2dad$ ligand[39].

The ruthenium centre resides in a slightly distorted square pyramidal coordination sphere with the hydride in the axial position, while the two nitrogen atoms and the centroids (ct) of the coordinated olefin units bind at the basal position. The long C–N distances (1.35 Å) and short C–C distance (1.38 Å) leave no doubt that the $trop_2dad$ ligand is present in its 1,2-enediamide[2] form, trop-N^--*CH*=*CH*-N^--trop (see **C**′ in Fig. 2) and the ruthenium centre remains in oxidation state +2.

The 16-valence electron complex **3** catalyses the transformation of MeOH and water into H_2 and CO_2 at temperatures below 100 °C under various conditions (Fig. 3b). In a simple apparatus containing a MeOH–water–tetrahydrofuran (THF) mixture and 0.5 mol% catalyst **3**, equipped with a reflux condenser (with circulating cooling fluid at −20 °C), ~80% conversion was achieved after 10 h with 1 g of MeOH. The dehydrogenation of MeOH was also performed in the presence of an inorganic base $M(OH)_2$ (M = Ca, Ba) and/or an amine (NEt_3) in a sealed Schlenk. The conversion was monitored by ^1H NMR spectroscopy using NEt_3 as an internal standard and gravimetric analysis of $BaCO_3$ or $CaCO_3$ to determine the amount of CO_2 generated. When the reaction was performed in a closed system, using 1 equiv. of NEt_3 and 1 equiv. of $Ba(OH)_2$ in a THF/water mixture at 90 °C, ~25% conversion of MeOH was reached. In this experiment, analysis of the gas phase after 10 h afforded only H_2 and no CO. The reaction can be performed in an apparatus open to air and the hydrogen produced has a sufficient purity to power a H_2/O_2 fuel cell (for details see Supplementary Section S3.1.b).

Assuming that the MeOH/H_2O mixture is converted according to reaction steps (1a)–(1c) and (2) as shown in Fig. 3b, additional experiments were performed to gain some insight into a possible reaction mechanism and ensure that formic acid (HCOOH) is an intermediate in the last stage of the reaction. The hydride complex **3** efficiently catalyses the decomposition of pure HCOOH (1 M solution dioxane) into H_2 and CO_2 at 90 °C within several minutes (Fig. 3c). Using 0.01 mol% of **3** as catalyst, initial turnover frequencies up to 24,000 h^{-1} were achieved. These are the highest values reported to date for a homogeneous ruthenium complex without addition of further additives[24]. Hydrogen was also rapidly evolved from a 5:2 mixture of HCOOH and NEt_3 under otherwise identical conditions.

Under the reaction conditions, no direct evidence was obtained for the dehydrogenation of methanol to formaldehyde (reaction (1a), Fig. 3b) or the dehydrogenation of methanediol to formic acid (reaction (1b), Fig. 3b), and a set of reactions with model substrates was performed. These reactions are presented in Fig. 5. Although anionic hydride complex **3** does not react rapidly with alcohols like MeOH, ethanol or benzylalcohol, it does react readily at room temperature with a slight excess of water or a carboxylic acid to form a new ruthenium complex **4**. Complex **4** is a highly reactive species and could not be isolated. The NMR data obtained indicate that the complex is diamagnetic and has C_{2v} symmetry. Specifically, in the ^1H NMR spectrum, a resonance at $\delta(^1H) = 8.4$ ppm is assigned to a proton bound to an imine group, –N=*CH*–, and one resonance at $\delta(^1H) = 4.59$ ppm to the four equivalent olefinic protons. These data compare well with the isoelectronic $[Rh(trop_2dad)]^+(OTf^-)$ (ref. 37). The cationic Rh(I) complex has a structure containing a 1,4-diazadiene ligand (**C** in Fig. 2 and $trop_2dad$ in Fig. 3a). The NMR resonances of the ^{13}C nuclei in **4** of the dad moiety ($\delta(^{13}C) = 147.5$ ppm versus 165.5 ppm in $[Rh(trop_2dad)]^+$) and the four equivalent olefinic resonances ($\delta(^{13}C) = 72.1$ ppm versus 85.3 ppm in $[Rh(trop_2dad)]^+$) indicate increased back-donation from the ruthenium centre into the diazadiene and olefinic groups and a significant contribution of resonance structure **4**′ to the electronic ground state of neutral $[Ru(trop_2dad)]$. At this stage, we refrain from a more detailed discussion of the electronic structure and assign an oxidation state to the ruthenium centre in **4**. For both Ru(0) and Ru(II), relatively few examples of tetra-coordinated complexes have been reported and these may have different spin states[40,41]. Adding triphenylphosphane (PPh_3) to the solution of **4** leads to the penta-coordinated complex **7** in high yield, which further bolsters the proposed structure for **4**. The 16-electron Ru(II) complex **7** has a distorted structure between a trigonal bipyramid and square pyramid with the $trop_2dad$ ligand in its enediamide form, trop-N^--*CH*=*CH*-N^--trop (for details see Supplementary Table S1 and Fig. S5). The *in situ* generated complex **4** was allowed to react with a slight excess of primary alcohols RCH_2-OH (R = Me, Ph) in THF. The reactions proceeded smoothly and, after 2 h at 65 °C, gave complexes **5** and **6**, respectively. Both complexes contain a zero-valent ruthenium centre and

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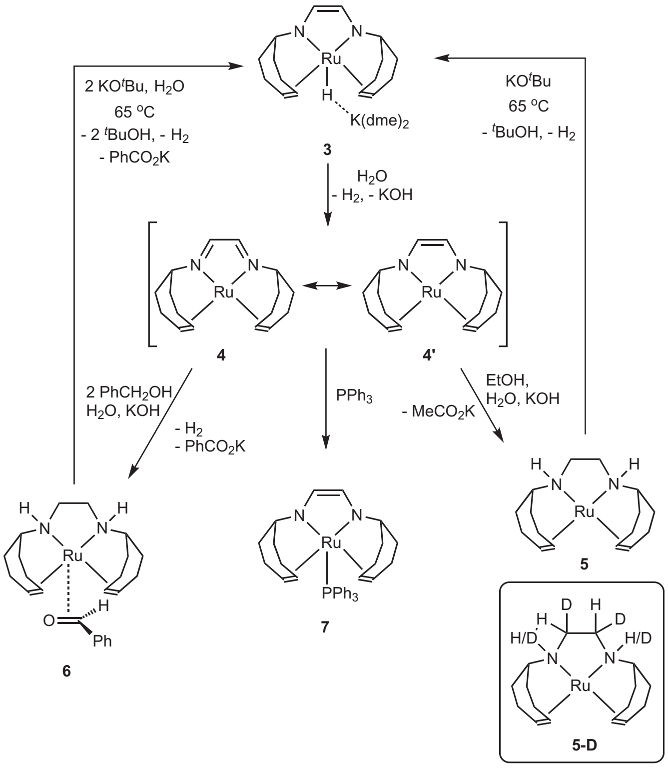

Figure 5 | Stoichiometric reactions with 3 leading to key intermediates 4, 4′, 5, 5-D and 6 in alcohol dehydrogenation reactions. Complex K[Ru(II)(H)(trop$_2$dad)] (**3**) reacts with a slight excess of water to form [Ru(trop$_2$dad] (**4**), which dehydrogenates alcohols (EtOH or BnOH, 4–10 equiv.) acting as hydrogen acceptor, to give the reduced complexes [Ru(0)(trop$_2$dae)] (**5**) or [Ru(0)(OCHPh)(trop$_2$dae)] **6**, which retains a dehydrogenated aldehyde molecule coordinated to the metal centre. With perdeuterated ethanol (D_3CCD_2OD), the partially deuterated complex **5-D** is obtained, indicating the chemical non-innocence of the trop$_2$dad ligand. Under basic conditions, complexes **5** or **6** lose dihydrogen (H_2) and revert to complex **3**. Highly reactive complex **4** can be trapped with triphenylphosphine (PPh_3) to form the stable pentacoordinated complex **7**.

the trop$_2$dae ligand with a fully hydrogenated diazadiene unit (Fig. 5). When the reaction was carried out with perdeuterated ethanol ($D_3C–CD_2–OD$), the partially deuterated complex **5-D** was obtained, indicating that the trop$_2$dad ligand of **3** participates actively in the dehydrogenation of the alcohol. The tetra-coordinated complex [Ru(trop$_2$dae)] (**5**) as well as the penta-coordinated complex [Ru(η^2-O=CHPh)(trop$_2$dae)] (**6**) with a side-on bound benzaldehyde ligand were fully characterized, including X-ray diffraction methods with single crystals. The molecular structures of **5** and **6** are displayed in Fig. 4b and c, respectively. Both complexes contain d^8-valence electron configured Ru(0) centres, which are stabilized by significant electron transfer from the metal to the π* orbitals of the coordinated olefin units (M → L back-bonding), as indicated by the rather long coordinated C4–C5 and C19–C20 bond distances (1.42–1.45 Å). The structural data show that the ligands in **5** and **6** are fully saturated. The C–N (1.48–1.51 Å) and C–C distances (1.52–1.53 Å) in the ligand backbone correspond to single bonds. The structure of complex **6** is best described as a distorted trigonal bipyramid with the η^2-aldehyde, one C=C$_{trop}$ unit and N1 in the equatorial plane, and N2 and the remaining C=C$_{trop}$ unit in the axial position[42]. The elongated C–O bond (1.311 Å) of the PhCH = O ligand indicates significant π back-bonding from the metal, which is enhanced by the conjugated phenyl group. Observation of the benzaldehyde complex **6** strongly indicates that in the alcohol dehydrogenation reactions catalysed by **3**, aldehydes are formed in the first step as proposed in reaction (1a) (Fig. 3b). We assume that replacing the phenyl group with the less electron-withdrawing and delocalizing methyl group in acetaldehyde gives a less stable adduct that dissociates to give Ru(0) complex **5**. This rare 16-valence electron configured d^8-Ru complex has a C_2 symmetric structure[43]. Under an atmosphere of argon, a solution of **5** in THF is remarkably stable for a prolonged period of time. The addition of 2 equiv. of KO^{t}Bu as a base promotes the loss of hydrogen and the regeneration of Ru(II) hydride complex **3**. Complex **6** undergoes similar conversion to complex **3** under comparable reaction conditions with 2 equiv. of base and a stoichiometric amount of water. The transformation of complex [Ru(trop$_2$dad)] (**4**) in **5** or **6**, as well the conversion of the benzaldehyde adduct **6** to the hydride complex **3**, are accompanied by elimination of dihydrogen and the formation of the corresponding potassium carboxylate. This observation is in accordance with the assumption that the dehydrogenation of alcohols proceeds stepwise as shown in Fig. 3b, reactions (1a–c). Computations (density functional theory) were carried out for the closely related reaction of primary alcohols with water to carboxylates, promoted by the Rh(I) amido complex [Rh(trop$_2$N)(PR$_3$)] (Fig. 1). These computations indicated that the dehydrogenation of hemiacetals—formed from aldehydes, RCH = O and water (reaction (1b))—to carboxylates (reaction (1c)) is faster than the dehydrogenation of alcohols to aldehydes and thereby excludes their direct observation. When the dehydrogenation of benzylalcohol is performed in $^{18}OH_2$ water, nearly fully ^{18}O-labelled benzoate is obtained as the product after 4 h at 65 °C with [K(dme)$_2$][Ru(H)(trop$_2$dad)] (**3**) as catalyst. Note that the exchange of oxygen atoms in benzoate is very slow

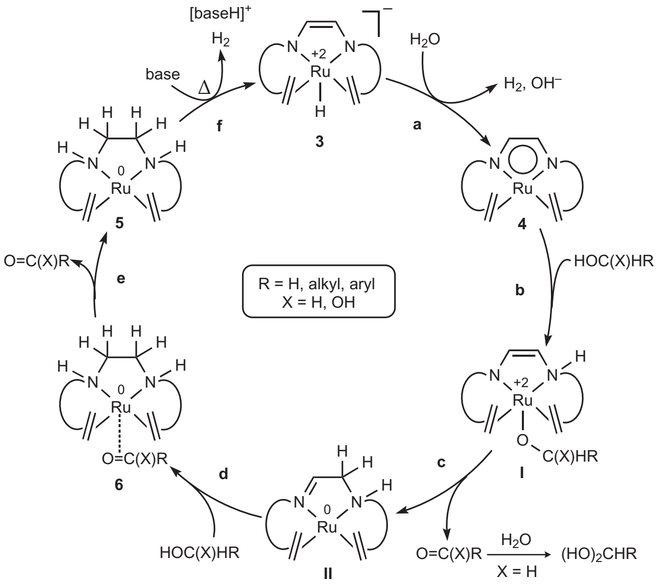

Figure 6 | Proposed simplified mechanism for the catalytic conversion of alcohols to carboxylic acids promoted by [Ru(II)(trop$_2$dad)] and [Ru(0)(tropdae)] complexes. a, The hydride ruthenate complex K[RuH(trop$_2$dad)] (**3**) reacts with water to give the neutral [Ru(tropdad)] species (**4**) under extrusion of the first equivalent of H_2. **b**, The hydroxyl group of a substrate molecule adds towards the Ru–N bond to form the Ru(+2) alkoxide **I** (not observed). **c**, An α-CH bond of the bound substrate is activated and transferred to one of the CH groups of the trop$_2$dad ligand backbone, giving reduced species **II**. **d**,**e**, This amino imino complex **II** may dehydrogenate another substrate molecule in a similar activation sequence to give complexes **6** and **5**. **f**, Finally, complex **5** thermally splits off another equivalent of H_2 under basic conditions whereby complex **3** is regenerated and the catalytic cycle is closed (step **f**). A basic, cut-down form of the trop ligand is shown for simplicity.

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(less than 5% after 3 h at 65 °C) without and in the presence of **3**. This experiment indicates that the incorporation of ^{18}O must occur during the formation of benzoate and not afterwards. Hence, it may be assumed that in the reversible hydration reaction of benzaldehyde with an excess of $^{18}OH_2$, the labelled hemiacetal $PhHC(^{18}OH)_2$ is obtained, which is subsequently catalytically dehydrogenated to $(PhC^{18}O^{18}O)K$.

Based on these experiments, we propose a simple working mechanism where the observed ruthenium complexes **3**, **4**, **5** and **6** are involved as catalytically active species for the conversion of MeOH and H_2O into formic acid and finally to H_2 and CO_2. Figure 6 highlights the electronic and chemical 'non-innocence' of the trop$_2$dad/trop$_2$dae ligand pair. In step (a), the hydride $[Ru(H)(trop_2dad)]^-$ (**3**) reacts with water to form the neutral $[Ru(trop_2dad)]$ complex **4** with the release of 1 equiv. H_2. In step (b), the hydroxyl group of a substrate molecule (alcohol, methandiol or formic acid) adds to the Ru–N bond to give the assumed intermediate **I**. The α-C–H bond of the coordinated substrate molecule is activated in step (c) by H transfer to one of the CH groups in the trop$_2$dad ligand backbone. In this process, the Ru(II) centre is reduced to Ru(0) to give a proposed amino imine complex **II**, and one molecule of a carbonyl compound (aldehyde, carboxylate, CO_2) is released. The amino imine complex **II** can react in a similar manner by addition of the polar O–H bond across the polar Ru–N bond and subsequent α-C–H bond activation to give Ru(0) complexes **6** (step (d)) and **5** under release of a second equivalent of a carbonyl compound (step (e)). Both **6** and **5** carry a hydrogenated trop$_2$dae ligand, which results from the formal uptake of 2 equiv. H_2. Finally, Ru(0) complex **5** is converted under the reaction conditions (base, elevated temperatures) to complex **3** (step (f)) and 1 equiv. of H_2, completing the catalytic cycle. This proposed mechanism involving steps (a) to (f) may be applied to alcohols, hemiacetals and formic acid (which contains a third α-CH group and is therefore finally decomposed into H_2 and CO_2).

Conclusions

A novel homogeneous catalytic system has been found for the clean conversion of methanol and water into hydrogen and carbon dioxide. The process is based on well-defined reaction steps and circumvents the formation of poisonous CO gas as by-product (avoiding inactivation of the molecular catalyst and contamination of the hydrogen fuel). During the catalytic cycle, the azadiene ligands reversibly store molecular hydrogen, and the oxidation states of the ruthenium centre shuttle between 0 and +2, facilitated by the electronically and chemically 'non-innocent' coordination environment. We believe these results may guide future research efforts, specifically in the immobilization of optimized molecular catalysts on conducting support materials for the development of electrodes for methanol-based fuel cells.

Received 3 November 2012; accepted 31 January 2013; published online 10 March 2013

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Acknowledgements

This work was supported by the Schweizer Nationalfonds (SNF), Eidgenössische Hochschule Zürich and the joint SNF/Deutsche Forschungsgemeinschaft research project ‘Unconventional Approaches to the Activation of Dihydrogen’ (FOR1175). H.G. thanks P. Edwards (University of Oxford) and Lotus Cars, in particular, for inspiration.

Author contributions

G.S-Q. performed the X-ray diffraction measurements with single crystals. All other authors planned and performed the experiments. R.E.R-L., M.T. and H.G. wrote the paper. All authors discussed the results and commented on the manuscript.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to M.T. and H.G.

Competing financial interests

The authors declare no competing financial interests.

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