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# A Diaminopropane Diolefin Ru(0) Complex Catalyzes Hydrogenation and Dehydrogenation Reactions.

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Homogeneous catalysis
Dehydrogenation
Hydrogenation
Ruthenium
Metal ligand cooperativity

**Phosphine-free Ru catalysts**: Tetradentate Ru(0) complexes with a diolefin diaminopropane or a dehydrogenated iminopropenamide ligand can be easily interconverted by

dehydrogenation or hydrogen transfer reactions. They have enabled the catalytic dehydrogenative coupling of alcohols and water or amines to the corresponding carboxylates and amides as well the reverse catalytic hydrogenation of carbonyl compounds.

A diaminopropane diolefin Ru(0) complex catalyzes hydrogenation and dehydrogenation reactions from @ETH and @IVIC<?_>official

New ruthenium (0) complexes with a cooperative diolefin diaminopropane (DAP) or the dehydrogenated iminopropenamide ligand (IPA) were synthesized for comparison with their diaminoethane (DAE)/ diazadiene (DAD) ruthenium analogues. These DAP/IPA complexes are efficient catalysts in dehydrogenation reactions of alkaline aqueous methanol which proceeds under mild conditions (T=70^°C) and of higher alcohols, forming the corresponding carbonate and carboxylates, respectively. The scope of the reaction includes an example of a 1,2-diol as model for biomass derived alcohols. Their catalytic applications are extended to the atom-efficient dehydrogenative coupling of alcohols and amines to amides. The reaction proceeds without any additives and is applicable to the synthesis of formamides from methanol. Moreover, DAP/IPA complexes catalyze the hydrogenation of a series of esters, lactone, ketone, activated olefin, aldehyde and imine substrates. The diaminopropane Ru catalyst exhibits higher activity compared to the dehydrogenated β-ketiminate (IPA) and previously studied DAD/DAE based catalysts. We present studies on their stoichiometric reactivity with relevance to their possible catalytic mechanisms and the isolation and full characterization of key reaction intermediates.

## Introduction

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Hydrogenation and dehydrogenation reactions are essential chemical transformations for manufacturing fine chemicals, foods, and fuels.[1] An increased need for hydrogen storage technologies has renewed the interest in acceptorless and reversible dehydrogenation processes of chemical compounds. Primary or secondary alcohols can be -- under specific catalytic conditions and by application of the principle of micro reversibility -- fully reversibly hydrogenated and dehydrogenated which make them one of the most attractive

hydrogen storage media.[2] The most promising liquid organic hydrogen carriers are based on methanol and polyalcohols derived from biomass.[3,4]

In the last decades, alcohol dehydrogenation reactions catalyzed in homogenous phase by catalysts containing noble metals (Ru,[5] Ir,[6] Rh,[7] or Re[8]) were intensively investigated. More recently, complexes with earth-abundant metals (Fe,[9] Co,[10] Cu,[11] Ni,[12] and Mn[13]) joined this flock. Previously, heterogeneous catalysts were applied in the reforming of aqueous methanol which moreover needed harsh conditions. Beller and Grützmacher proposed independently Ru complexes which contain a cooperative aliphatic PNP or diazadiene ligand, respectively. These complexes were able to dehydrogenate aqueous methanol fully according to: $H_3COH+H_2O \rightarrow 3\ H_2+CO_2$ under atmospheric pressure and T<100^°C.[14] There is convincing evidence that these reactions proceed step-wise with formaldehyde and formic acid as intermediates. In related work, the direct conversion of higher primary alcohols to carboxylates in a dehydrogenative process was successfully accomplished by the pioneering work of Milstein *et^^al.*, using Ru-PNN based catalysts.[15] Recently, other pincer or N-heterocyclic carbene (NHC) complexes with Ru,[16] Ir[17] and Fe[18] as metals have been investigated in the dehydrogenative coupling of alcohols and water. Conversion of polyols containing 1,2-diols has proven to be a difficult process and very few examples are known,[19] which mainly focus on the conversion of glycerol to lactic acid (LA).[17,18] Milstein *et^^al.* also pioneered the dehydrogenative coupling of alcohols and amines to the corresponding amides and this new "green" process was subsequently applied to the synthesis of polymeric materials.[20] Meanwhile numerous metal complexes are able to catalyze this dehydrogenative amidation reaction,[21] although there are still some limitations with respect to the substrate scope. Merely four catalytic systems are able to convert methanol and amines to formamides in the absence of harsh oxidative conditions.[22] Only one catalyst, an aliphatic Fe-PNP[22d] complex, exhibits a TON>50 and is only active with selected secondary amines. Progress in alcohol dehydrogenative processes seems to be coupled to the

development of new ligand frameworks likely due to the fact that in almost all cases they play a relevant role in substrate activation. Figure^^1<figr1> illustrates this metal ligand cooperation. The cooperative sites can be located in the first coordination sphere (for example metal coordinated amine/amido and hydroxy/carbonyl functions), or in a remote position like in M-PNN and M-PNP pincer complexes, which undergo a reversible aromatization and dearomatization transformation. Alternatively, they involve redox and chemical non-innocent behavior as in diazadiene/diaminoethane complexes which are interconverted by hydrogenation-dehydrogenation and intramolecular redox processes.[23]

The reverse process, the catalytic reduction of carboxylic acid derivatives has also witnessed a rapid development. Ester hydrogenation is especially relevant in the context of upgrading of bio-based feedstock. It is also a key step in the "green" production of methanol by hydrogenating methyl formate (derived from $CO_2$ or CO) to methanol.[24] These reactions, involving molecular hydrogen as the reducing agent, can be promoted by heterogeneous and homogeneous catalysts. Current heterogeneously catalyzed processes are operated at harsh conditions (200--300^°C and $H_2$ pressures of 140--300^^bar)[25] and are frequently accompanied by side reactions and product degradation. Homogeneous catalysts can operate at significantly lower temperatures, thereby allowing for high selectivity and are more suitable when highly functionalized substrates need to be converted. They are also much more easily tuned to achieve a better performance. One relevant example concerns the previously mentioned Ru PNN complex reported by Milstein *et^^al.*[26] This pincer complex was modified by placing one (CNN)[27] or two carbene groups (CNC)[28] on the ligand to give a superior catalyst. The presence of the cooperative amine function in the first coordination sphere of the metal center (see archetypical Noyori-type complexes) typically results in more active ester hydrogenation catalysts when compared to these pincer-type systems.[29] We have also demonstrated the cooperative role of an amino/amido functions in a rhodium(I) amino bis (olefin) complex in hydrogenation and transfer-hydrogenation reactions.[30] The most active

ester hydrogenation catalysts are obtained with metal complexes containing amino-pincer ligands with three donor groups attached to the metal in a meridional fashion.[31] Currently, the best catalysts for the hydrogenation of esters were reported by Gusev *et al* who reported a series of Ru and Os PNN and SNS pincer complexes achieving high turnover numbers (TON's) under remarkably mild conditions.[32]

The development of an efficient and generally applicable homogeneous catalytic system for reversible dehydrogenation-hydrogenation reactions of alcohols remains of great interest. This goal may be reached by a proper design of a multifunctional cooperative ligand which not only stabilizes the catalytic intermediates but also actively participates on substrate binding and activation. In previous studies, the [Ru(trop$_2$DAD)] complex **2** (trop$_2$DAD=1,4-bis(5H-dibenzo[a,d]cyclohepten-5-yl)-1,4-diazabuta-1,3-diene), which can be described by two resonance structures with either a Ru(0) or a Ru(II) center, reacts with an alcohol (methanol, ethanol or benzyl alcohol) to form a Ru(0) complex **1**, which "stores" up to two equivalents of $H_2$ in the diazadiene ligand backbone.[14b] Dehydrogenation of complex **1** releases two equivalents of $H_2$ to regenerate complex **2**. Initial assumptions involved both complexes as active intermediates in the catalytic cycle, but recent findings supported by DFT calculations indicate that they may be independent catalysts, with different mechanistic pathways, but linked by a chemical equilibrium.[33]

**Results and Discussion**

In order to study these phenomena of ligand non-innocence specifically in Ru(0)/Ru(II) complexes in deeper detail, we envisioned to expand the ethylene bridge between the two nitrogen centers in complexes **1** or **2** by an additional methylene group. The diaminopropane ligand trop$_2$DAP was synthesized according to the reaction sequence shown in Scheme^^1<schr1>, which consists in a straightforward initial reductive amination of dibenzosuberenone. $^1$H NMR spectroscopic analysis of the ligand in solution revealed the

presence of three conformers. In the solid state, the amine bound trop substituents adopt an endo/exo conformation (See Figure^^2<figr2>A). Reaction of the trop$_2$DAP ligand with the ruthenium precursor complex [RuCl$_2$(PPh$_3$)$_3$] led to the formation of the diamine Ru(II) complex [RuCl$_2$(trop$_2$DAP)] **3-(Cl)$_2$** which can be converted to the zerovalent Ru complex [Ru(trop$_2$DAP)] **3** with a 16 valence electron configuartion by direct reduction with Mg (Scheme^^1<xschr1>). Alternatively, a combination of base and superhydride can be used to give **3** in a higher yield (87^%). The reaction must be performed at low temperature since the coordinated ligand can be thermally dehydrogenated. In the presence of a strong base (KHMDS or KO*t*Bu) at 70^°C, complex **3** eliminates in solution 2.5 equivalents of hydrogen in an open vessel flushed with Ar. In this reaction, both NH groups become deprotonated and the propylene bridge loses three hydrogens to yield the salt K[Ru(trop$_2$IPA)] **4**, in which formally a mono-anionic β-diketiminate ligand is coordinated to a Ru(0) center (Scheme^^2<schr2>a).[34]

In the absence of base, when **3** is heated in toluene under reflux it slowly converts (4^^days) to the pentacoordinated ruthenium (II) complex **5**. This species is best described with mono-anionic β-diketiminate and a hydride ligand resulting from a formal elimination of 2 equivalents of $H_2$ and migration of one hydrogen atom from the ligand backbone to the metal center (Scheme^^2<xschr2>a). $^1$H NMR spectra of both complexes, **4**[33] and **5**, exhibit similar $^1$H NMR data for the ligand backbone in the region of aromatic protons. In addition, complex **5** shows resonances at rather high frequencies for the olefinic protons at δ($^1$H)=4.09 (dd) ppm and a signal for the hydride at δ($^1$H)=<M->14.8 (s) ppm. The corresponding spectrum of complex **3** exhibits the proton signals of the saturated backbone in the δ($^1$H) range of 3.3--1.5^^ppm, which is close to the free ligand, and protons of the coordinated olefins at low frequencies [δ($^1$H)=1.85 (d) and 1.71 (d) ppm]. A series of stoichiometric reactions were performed to study the reactivity of complexes **3** and **4** towards water or an alcohol, either under neutral or basic conditions (Scheme^^2<xschr2>). In the reaction with

neutral water, complex **3** is converted to the octahedral hydrido hydroxo Ru(II) complex **6**, while in an alkaline solution, the reaction leads additionally to the formation of the dehydrogenated complex **5** as minor product. Water is able to protonate complex **4** forming the hydride species **5** in nearly quantitative yield and only complex **3** is detected as minor side product. Addition of a strong reductant ($KC_8$) to a THF-$d_8$ solution of **5** reverses this reaction and yields **4** again. While the dehydrogenation of the DAP backbone proceeds smoothly under basic conditions or by simply heating the complex in a flask which allows the release of gaseous products ("open" reaction system), ligand transfer hydrogenation with an alcohol as hydrogen source is significantly more difficult. The reaction of a solution of complex **4** in THF with benzyl alcohol or 1,2-propanediol at 50^°C and in a closed system leads to the formation of complex **3** in low yield (12^% by NMR), in both cases. The reaction of an excess of 1,2-propanediol and water with complex **3** in benzene at higher temperature resulted in the formation of the hexacoordinated lactate complex **7** in more than 80^% yield. In this complex the fully hydrogenated form of the DAP ligand remains intact (see Figure^^2<xfigr2>D). The reaction of complex **7** with base at room temperature liberates the lactate salt and regenerates **3** quantitatively.

The reactivity of complex **3** in the presence of methanol was also investigated under anhydrous or aqueous conditions. All the experiments were performed at moderate temperatures (35--50^°C). In the absence of water, the complex reacts with the O<C->H bond of methanol forming the stable hydrido methoxy complex **9** as mayor product. The dicarbonyl complex **8** which contains two carbonyl groups in the coordination sphere of the metal, is formed as a minor product (10^%). The formation of the latter is likely due to the fact that in absence of water formaldehyde is formed as first dehydrogenation product in sufficiently high concentration, which is then decarbonylated.[35]A comparable observation was made when $trop_2$dad complexes like **2** were reacted with aqueous formaldehyde solutions.[36] In the presence of water, formaldehyde will be immediately hydrated and in this case, the reaction

proceeds further to give carbonate as fully dehydrogenated product. Indeed, we were able to isolate single crystals of two carbonate complexes **10** and **11** formed as mayor products when different ratios of methanol: water was used. In the presence of an excess of methanol-water in a ratio 2^:^1, the dinuclear hydrido carbonate complex **10** is formed together with the hydroxo complex **6** in 1^:^1 ratio. When the ratio of methanol was increased with respect to water and complex **3**, the main product isolated was the mononuclear hydrido methylcarbonate ruthenium complex **11**. This species is a particularly unstable complex and when a solution in THF is evaporated under reduced pressure or heated at 65^°C for a short period of time, it decomposes forming the methoxide complex **9** and $CO_2$. To discard a possible formation of complex **9** and insertion of adventitious $CO_2$ into the metal-O bond, we performed the reaction with labelled $^{13}CH_3OH$ and validated the incorporation of labeled carbon in the carbonate product **11** and the subsequent release of $^{13}CO_2$.

The molecular structures of compounds **3** (Scheme^^1<xschr1>), and **4**,[34] **6**, **7**, **8**, **9**, **10**, and **11** (Scheme^^2<xschr2>) were determined by X-ray diffraction methods using a single crystal of each compound. Plots of the structures are shown in Figure^^2<xfigr2>. The structure of complex **3** (Figure^^2<xfigr2>b) shows a close binding interaction between the Ru center and the two amino and two olefin groups. The coordination sphere around the metal center is almost planar [ϕ=11.4(1) of the planes defined by both N<C->Ru-ct, ct=centroid as centroid of the C<C=>$C_{trop}$] as expected for a $d^8$-metal center with two π-accepting and two σ-donating binding sites each in *cis*- and mutually in *trans*-position.[37] The bonding parameters and coordination geometry in **3** closely resemble those of the previously reported DAE complex **1**. Metal-to-ligand π-backdonation from the d-orbitals at the metal to the π∗-orbitals of the olefins significantly elongates the C<C=>C bonds to 1.433(3) Å compared to those in the free ligand [1.338(3) Å]. The bond lengths within the propyl-backbone are similar to those of the 1,3-diaminopropane molecule. As previously reported,[34] the Ru species **4** shows a slightly distorted square-planar structure [ϕ=+13.2(1)°] and as such resembles other

β-diketiminato ("NacNac") Ru complexes with a fully dehydrogenated planar backbone and roughly symmetrical bonds. When comparing complexes **3** and **4**, one can observe that **4** binds much more tightly to the nitrogen atoms with bond distances significantly shorter than in complex **3** [2.178(2) Å and 2.192(2) Å for **3** versus 2.057(1) Å and 2.056(1) Å for **4**]. However, this shorter bonding is not replicated in the Ru-ct, where complex **3** actually features shorter distances [1.990(2) Å and 1.987(2) Å for **3**, and 1.999(1) Å and 2.005(1) Å for **4**]. Complex **4** shows comparable backdonation into the olefins to **3**, if measured by the elongation of the coordinated olefins, albeit more symmetrically distributed [1.433(3) Å and 1.446(3) Å for **3**, and 1.448(2) Å and 1.444(2) Å for **4**]. The largest difference is present in the bond distances located in the backbone of the trop-ligand. Here the transformation of the C*H*$_2$ groups into methylidyne groups results in a significant bond shortening from 1.483(3) Å, 1.516(3) Å, 1.512(3) Å, and 1.489(3) Å along the N-$(CH_2)_3$-N backbone of **3** to 1.327(2) Å, 1.391(2) Å, 1.396(2) Å, and 1.326(2) Å along the backbone of **4**. Both the distances between backbone atoms and those between metal center and imines are remarkably shortened, suggesting a delocalized metalloaromatic system.[38]

All complexes **7--11** preserve a hydrogenated diaminopropane ligand and with exception of the dicarbonyl species **8**, in all cases the whole tetradentate ligand remains coordinated to the metal. Complex **8** features the longest C<C=>$C_{trop}$ bond out of all the complexes with 1.463(6) Å. The uncoordinated double bond measures 1.344(6) Å which, expectedly, is comparable to that of the free ligand. It also features the longest Ru<C->N bond with 2.278(3) Å on the uncoordinated side. It is interesting to note that complexes **6** through **11** (with the exception of **8**) all have Ru<C->N bonding that is shorter than that of **3**. For the Ru-ct bonding, complexes **6** to **11** all feature significantly longer bonds [2.010(6)--2.065(7) Å] than both **3** and **4** [1.987(2)--2.005(1)Å], presumably due to the additional substituents causing additional steric bulk around the metal center. It may also be the reason for which complexes **6**, **7**, **9**, **10**, and **11** have smaller torsion angles around the metal center

and deviations from a planar structure. Complex **6** and **9** have the smallest angles ϕ of 0.1(1) and 0 (due to symmetry), respectively. Complexes **7**, **10**, and **11** have slightly higher distortions but not as severe as in **3** and **4**. The elongation of the C<C=>$C_{trop}$ groups when compared to those of the free ligand is apparent in all of the presented complexes. We previously published the complex [Ru($trop_2$DAD)($PPh_3$)(CO)] and its role as an intermediate in the catalytic dehydrogenation of aqueous formaldehyde.[36] Complex **8** closely resembles the mentioned ruthenium complex since both feature a bridged trop-type ligand that is only partially coordinated and CO as a further ligand. Both complexes appear in a distorted trigonal bipyramidal structure where the axial positions are occupied by an amine and a carbonyl ligand. Complex **8** has tighter bonding to the trop double bond [2.023(3) Å versus 2.068(2) Å] and stronger backdonation from the metal, resulting in a slightly more elongated C<C=>$C_{trop}$ bond [1.463(6) Å vs.1.445(5) Å]. The axial Ru-CO bond distance in **8** is shorter [1.830(4) Å versus 1.857(4) Å)] as well the CO bond [1.156(5) Å versus 1.166(4) Å]. Pertinent interatomic distances and angles are given in Figure^^2<xfigr2> and Tables^^S11 and S12 in the supporting information.

The results obtained in stoichiometric experiments, encouraged testing of complexes **3** or **4** as catalysts for the dehydrogenative coupling of alcohols and water to carboxylic acids. A comparison of the catalytic activity of complexes **1--4** is shown in Table^^1<tabr1>. In an initial screening, the reaction was performed in the absence of an organic co-solvent. Table^^1<xtabr1> shows that the catalytic performance between the complexes with saturated backbone (**1** and **3 -** entries^^1, 3) versus those with an unsaturated backbone (**2** and **4 --** entries^^2, 4) is relatively small but in favour of **1** and **3** by 16--19^%. While complexes **1**, **3** and **4** were tested without additional co-solvent, complex **2** was tested using dioxane, due to its lower solubility in an aqueous solution. We have also tested all complexes (**1--4**) using toluene as co-solvent. Under these conditions, complexes **1** and **2** where practically inactive (entries^^5 and 6) while complexes **3** and **4** show similar high activity, with a slight

preference for complex **3** (entries^^7 and 8). Complexes **1** and **2** remain insoluble when toluene is used as co-solvent. Turnover frequencies (TOF) after 1, 3 and 24^^h in water-toluene mixtures indicate that complex **4** is a slightly better catalyst that complex **3** (see entries^^5--8 in Table^^1<xtabr1>). After 24^^h the conversion rate drops probably because the β-ketiminate derivative shows lower stability under these reaction conditions.

The best conditions were obtained with 0.5^^mol% of the zero-valent complexes [Ru(trop$_2$DAP)] **3** or K[Ru(trop$_2$IKA)] **4** in a mixture of water and toluene as solvent and at T=120^°C (entries^^7 and 8, Table^^1<xtabr1>). We have also tested the catalytic activity of the precursors **3-Cl$_2$** and [RuCl$_2$(PPh$_3$)$_3$] (entries^^9 and 10, Table^^1<xtabr1>) under the optimal conditions applied with catalysts **3** and **4**. These control experiments confirmed the essential role of the tetradentate ligand (entry^^9) and the preference for a fully reduced catalyst (entry^^10). We have also tried to identify the nature of the Ru complex after the catalytic dehydrogenation of benzyl alcohol reaction ceded using a slightly higher catalyst load (1^^mol%). Analysis of the reaction mixture shows that there is only one ruthenium complex present in the organic phase (toluene). This complex was identified as benzoate hydride complex [RuH(O$_2$CPh)(trop$_2$DAP)] (**7-Bz**) which was characterized spectroscopically and has a structure similar to complex **7**. The composition of **7** is further confirmed by MALDI-FT-ICR (See Supporting Information). With optimized reaction conditions established (entry^^7, Table^^1<xtabr1>), we investigated the versatility of catalyst **3** in the DHC reaction of several alcohols. As Table^^2<tabr2> shows, benzyl alcohol (entry^^1) and aliphatic alcohols (entries^^2 and 3) were converted with about the same efficiency. 2-Furoic acid was isolated in rather low yield (35^%, entry^^4). The reaction with 1,2-propanediol as substrate led to the formation of lactate in acceptable yield (55^%) but required an increased catalyst loading of 2^% (entry^^5, Table^^2<xtabr2>). Complex **4** was also tested in the catalytic conversion of this substrate, but disappointingly gave a very low yield of product (entry^^6). In our previous stoichiometric studies with complex **3**, facile dehydrogenation of

aqueous methanol at T<60^°C and the formation of carbonate complexes was observed (**10** and **11** in Scheme^^2<xschr2>) without adding a base. Moreover, decarboxylation of the carbonate compound **11** under release of $CO_2$ and $H_2$ and formation of complex **9** occurred quantitatively under mild conditions. These observations prompted us to test the catalytic reforming of aqueous methanol without further additives and under mild conditions. Indeed, complex **3** is able to catalyze the complete dehydrogenation of MeOH to 3 equivalents of $H_2$ and $CO_2$ at 60^°C, achieving a TON of up to 102.

For the exploration of the scope and limitation of the catalytic system in the direct synthesis of amides from amines and alcohols, 1^^mol% of catalyst **3** was reacted in toluene as solvent at T=120^°C (Table^^3<tabr3>). Excellent yields of amides were obtained from the reaction of sterically unhindered alcohols and amines, including the intramolecular amidation using 5-aminopentanol (entries^^1--8, Table^^3<xtabr3>). In the amidation of methanol with 1-aminohexane, 86^% isolated yield of the corresponding formamide (entry^^1) were obtained which is a significant improvement over previously reported catalytic reactions with primary amines.[22] The reaction of benzyl alcohol with aliphatic amines bearing a substituent in α-position or aniline afforded lower yields (52--63^%) of the corresponding amide (entries^^9--11, Table^^4<tabr4>). Secondary amines are not converted (entries^^12 and 13). These results indicate that the ruthenium-catalyzed direct amide formation is clearly sensitive to steric hindrance. The transformation using a chiral amine proceeds under retention of the stereo-center (entry^^9).

After these successful catalytic dehydrogenation reactions, the activity of complex **3** as catalyst for hydrogenation reactions was studied as well (Table^^4<xtabr4>). With 0.05^^mol% of catalyst, 8^^atm of $H_2$, and toluene at 80^°C, the cyclic ester given in entry^^1 is cleanly converted to the corresponding dihydroxy compound. Hydrogenation of methyl formate is rather challenging, and in THF at 65^°C only 14^% conversion (TON=280)

was achieved (entry^^2). The conversion was improved significantly to a TON of 1'000, in toluene at 80^°C (entry^^3). The hydrogenations of butyl butyrate and methyl benzoate proceed with moderate yields (entries^^4 and 5). For methyl benzoate, benzaldehyde was detected in less than 1^% and transesterification of benzyl benzoate took place with ca. 7^% yield. Amides, either primary or secondary, are not hydrogenated under these reaction conditions (entries^^6 and 7), which is of interest for chemoselective hydrogenations of compounds in which both, ester and amide functions, are present. Indeed, the methyl pyrrolidencarboxylate was cleanly and selectively hydrogenated to the corresponding alcohol, while the amide moiety was not reduced (entry^^8). The tolerance of the presence of some additional functional groups was investigated. Ethyl levulinate, which contains an additional keto group in β-position (entry^^9), was preferentially hydrogenated at the keto function and under the reaction conditions 71^% ethyl 4-hydroxypentanoate and only 29^% of the fully hydrogenated product 1,4-pentanediol/ethanol was obtained. Consequently, the aldehyde function in hydroxymethylfurfural (HMF), a platform molecule from biomass,[39] was reduced to 2,5-bis-(hydroxymethyl)furan (DHMF) in 52^% isolated yield (entry^^10). This process is of interest because HMF can be obtained directly from lignocellulosic biomass and DHMF is a valuable precursor for polymeric materials.[40] Dimethyl itaconate, which contains an ester and an additional α,β-unsaturated ester function, was hydrogenated under the uptake of three equivalents of $H_2$ to 2-methyl-1,4-butanediol with excellent yield (entry^^11). Finally, the hydrogenation of an imine was successfully achieved with excellent yield (entry^^12).

## Conclusions

A new $d^8$-valence electron configured Ru(0) catalyst [Ru(tropN$(CH_2)_3$Ntrop)] (**3**) which has no phosphine function is an active catalyst for the dehydrogenative coupling of alcohols with water or primary amines to give the corresponding carboxylates or amides, respectively. No further additives are needed. The principle of microscopic reversibility

implies that **3** may also be an efficient hydrogenation catalyst. While this has not been observed for amides up to 80^°C and 8^^atm of $H_2$, other carbonyl functions such as aldehydes, ketones, and esters are hydrogenated under neutral and mild conditions (low $H_2$ pressure and temperature). Also C<C=>N bonds in imines are hydrogenated to the corresponding amines. Methyl formate and HMF, both challenging substrates, are converted although with lower efficiency.

The 1,3-diaminopropane moiety in complex **3** undergoes dehydrogenation forming a β-ketiminate ligand under thermal conditions in the presence or absence of base.[23] The process is reversible and complex **4** can be converted to **3** by hydrogen transfer reaction with an alcohol as hydrogen source. Although we cannot discard the direct participation of both complexes in the same catalytic cycle, most likely, both are catalysts on different reaction pathways as previously calculated for related complexes with a saturated DAE or unsaturated DAD ligand (Scheme^^3<schr3/o>).[33,36,41] Here we propose that dehydrogenation of the substrate (alcohol, hemiacetal or hemiaminal) by complex **4** occurs via a Noyori-Morris-type mechanism to form complex **4**^**A**, as previously proposed for the DAD complex **2**.[33] Subsequent dehydrogenation of this intermediate could occur directly or via substrate/solvent-assisted pathways to close the cycle. A different mechanism is proposed for complex **3**, which undergoes a rearrangement to form the hydride complex **3'** containing a Ru(II) center. Initial dehydrogenation of an alcohol by complex **3'** would form the active species **3**^**A**. This alkoxide intermediate will start the catalytic cycle via a metal-centered pathway leaving the ligand nitrogen (DAP) in a protonated state throughout the entire cycle. Note that the isolation of the methoxide complex **9**, carboxylate complexes **7** and **7-Bz** and carbonates **10** and **11** support this assumption. But we note that both proposals are highly speculative and are simply based on previous studies with complexes **1** and **2**. Further mechanistic studies are required to gain insight into these very complex reaction mechanisms which are currently in

progress. Additionally, a detailed kinetic investigation will be accomplished and reported in due course."

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## Conflict of Interest

The authors declare no conflict of interest.

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Figure^^1 a) Metal ligand cooperativity in catalyzed dehydrogenation and hydrogenation processes. b) Milstein's PNN pincer, Beller's PNP catalyst, and an amide Rh(I) complex. The chemical and redox non-innocent behavior of Ru DAE / Ru DAD complexes (**1** and **2**) and the new Ru DAP/Ru IPA complexes (**3** and **4)**. Cooperative sites of the ligands are indicated in blue.

Figure^^2 ORTEP drawings of the molecular structure of trop$_2$DAP (a), **3** (b), **6** (c), **7** (d), **8** (e), **9** (f) **10** (g) and **11** (h). Thermal ellipsoids are drawn at a 50^% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. ct1 and ct2 are the centroids of the C<C=>C bonds C4<C->C5 and C19<C->C20 respectively. ct3 and ct4 are the centroids of the C<C=>C bonds C37<C->C38 and C52<C->C53 respectively Selected bond distances [Å] and angles [°]: a) trop$_2$DAP: C4<C->C5 1.338(3), C19<C->C20 1.347(2), N1<C->C31 1.471(2), C31<C->C32 1.523(2), C32<C->C33 1.517(2), C33<C->N2 1.471(2). b) **3**: C4<C->C5 1.433(3), C19<C->C20 1.446(3), Ru1<C->N1 2.178(2), Ru1<C->N2 2.192(2), Ru1<C->ct1 1.990 (2), Ru1<C->ct2 1.987(2); N2<C->Ru1<C->N1 89.3(1), N1<C->Ru1<C->ct1 89.2(1), N2<C->Ru1<C->ct2 89.6(1). c) **6**: C4<C->C5 1.425(7), C19<C->C20 1.429(7), Ru1<C->N1 2.157(5), Ru1<C->N2 2.154(4), Ru1<C->ct1 2.043(5), Ru1<C->ct2 2.010(6), Ru1<C->O1 2.140(4), Ru<C->H1 1.47(5); N2<C->Ru1<C->N1 90.3(2), N1<C->Ru1<C->ct1 87.9(2), N2<C->Ru1<C->ct2 88.7(2), O1<C->Ru1<C->H1 154(2); d) **7**: C4<C->C5 1.412(3), C19<C->C20 1.417(3), Ru1<C->N1 2.148(2), Ru1<C->N2 2.158(2), Ru1<C->ct1 2.054(2), Ru1<C->ct2 2.042(3), Ru1<C->O1 2.226(2), Ru<C->H1 1.51(2); N2<C->Ru1<C->N1 87.5(1), N1<C->Ru1<C->ct1 89.3 (1), N2<C->Ru1<C->ct2 89.3(1), O1-Ru1-H1 165.1(1). e) **8**: C4<C->C5 1.344(6), C19<C->C20 1.463(6), Ru1–N1 2.278(3), Ru1<C->N2 2.211(3), Ru1<C->ct2 2.023(4), Ru1-C34 1.830(4), Ru<C->C35 1.899(4), C34-

O1 1.156(5), C35-O2 1.157(5) Ru<C->H1 1.51(2); N2<C->Ru1<C->N1 85.1(1), N2<C->Ru1<C->ct2 86.6(1), C34-Ru1-C35 88.5(2). f) **9**: C4<C->C5 1.431(4), N1<C->C16 1.487(2), C16<C->C17 1.516(2), Ru1<C->N1 2.172(1), Ru1<C->ct1 2.042(1), Ru1<C->O1 2.192(3), Ru<C->H1 1.45(4); N1<C->Ru1<C->N1' 90.2 (1), N1-Ru1-ct1 88.0(1), O1<C->Ru1<C->H1 158.0(9). g) **10**: C4<C->C5 1.405(7), C19<C->C20 1.406(7), Ru1<C->N1 2.154(4), Ru1<C->N2 2.140(4), Ru1<C->ct1 2.042(4), Ru1<C->ct2 2.054(5), Ru1<C->O1 2.211(3), Ru<C->H1 1.60(4), O1<C->C34 1.252(6), C34<C->O2 1.229(7), C34<C->O3 1.368(7), O3<C->C35 1.426(7); N2<C->Ru1<C->N1 86.9(2), N1<C->Ru1<C->ct1 89.0(2), N2<C->Ru1<C->ct2 89.8(2), O1<C->Ru1<C->H1 167(1), O1<C->C34<C->O2 128.8(5), O2<C->C34<C->O3 115.3(5), C34<C->O3<C->C35 116.3(4). h) **11**: C4<C->C5 1.41(1), C19<C->C20 1.41(1), Ru1<C->N1 2.163(5), Ru1<C->N2 2.168(5), Ru1<C->ct1 2.064(7), Ru1<C->ct2 2.039(7), C37<C->C38 1.39(1), C52<C->C53 1.41(1), Ru2<C->N3 2.162(5), Ru2<C->N4 2.176(5), Ru1<C->ct3 2.065(7), Ru1<C->ct4 2.061(7), Ru1<C->O1 2.249(4), Ru<C->H1 1.58(5), Ru2<C->H2 1.57(4), Ru2<C->O2 2.254(4), O1<C->C67 1.302(8), C67<C->O2 1.298(8), C67<C->O3 1.265(8); N1<C->Ru1<C->N2 89.7(2), N1<C->Ru1<C->ct1 87.9(2), N2<C->Ru1<C->ct2 88.6(2), O1-Ru1-H1 162(3), N3<C->Ru2<C->N4 90.7(2), N3<C->Ru2<C->ct3 87.9(2), N4<C->Ru2<C->ct4 87.3(2), O2<C->Ru2<C->H2 158(2), O2<C->C67<C->O3 122.2(6), O3<C->C67<C->O1 121.8(6).

Scheme^^1 Synthesis of trop$_2$DAP ligand and coordination to ruthenium.

Scheme^^2 a) Interconversion of complexes **3** and **4** and their reactivity towards water. b) Summary of stoichiometric experiments of complex **3** with aqueous 1,2-propanediol or methanol and under anhydrous conditions.

Scheme^^3 Proposed mechanisms of alcohol dehydrogenation catalyzed by complexes **3** or **4**.

Table^^1 Catalyst screening for the catalyzed DHC of benzyl alcohol and water.<W=3>

<forr1>

| Entry | Catalyst | Solvent | TOF [h$^{<M->1}$] | | | Yield [%][a] |
|---|---|---|---|---|---|---|
| | | | 1^^h | 3^^h | 24^^h | |

| | | | | | | |
|---|---|---|---|---|---|---|
| 1 | **1** | $H_2O$ | -- | -- | -- | 81 |
| 2 | **2** | $H_2O$/dioxane | -- | -- | -- | 65 |
| 3 | **3** | $H_2O$ | -- | -- | -- | 87 |
| 4 | **4** | $H_2O$ | -- | -- | -- | 68 |
| 5 | **1** | $H_2O$/toluene | 1 | 0.6 | 0.2 | <5 |
| 6 | **2** | $H_2O$/toluene | 7 | 4 | 0.5 | 6 |
| 7 | **3** | $H_2O$/toluene | 14.5 | 10.4 | 4.6 | 90 |
| 8 | **4** | $H_2O$/toluene | 12.6 | 16.1 | 3.7 | 86 |
| 9 | **$RuCl_2(PPh_3)_3$** | $H_2O$/toluene | -- | -- | -- | <5 |
| 10 | **3-$Cl_2$** | $H_2O$/toluene | -- | -- | -- | 56 |

[a] NMR yields of potassium benzoate for reactions conducted on 10^^mmol scale of BnOH (1.0^^equiv), KOH (1.1^^equiv), [Ru] (0.5^^mol%) in water (5^^mL) or mixtures with toluene or dioxane (2^^mL), during 48^^h at 120^°C.

Table^^2 Catalyzed oxidation of primary alcohols to carboxylic acids[a].<W=3>

<forr2>

| Entry | <forr3> | Product | Catalyst [mol^%] | Isolated yields [%] |
|---|---|---|---|---|
| 1 | <forr4> | <forr5> | **3** (0.5) | 75 |
| 2 | <forr6> | <forr7> | **3** (0.5) | 72 |
| 3 | <forr8> | <forr9> | **3** (0.5) | 68 |
| 4 | <forr10> | <forr11> | **3** (0.5) | 35 |

| | | | | |
|---|---|---|---|---|
| 5 | <forr12> | <forr13> | **3** (2) | 55[b] |
| 6 | <forr14> | <forr15> | **4** (2) | 7[b] |

[a] Reaction conditions: alcohol (1.0^^equiv), water/toluene (2.5^:^1, 1.4^^M), KOH (1.1^^equiv), reflux, 48^^h, [b] A mixture of water/toluene (4^:^1, 0.4^^M) was used. Other products detected in this reaction include potassium acetate and polylactic acid

Table^^3 DHC of primary alcohols and amines to amides catalyzed by **3**.<W=3>

<forr16>

| Entry | <forr17> | <forr18> | <forr19> | Yield [%][a] |
|---|---|---|---|---|
| 1 | $CH_3OH$ | <forr20> | <forr21> | 86 |
| 2 | $CH_3CH_2OH$ | <forr22> | <forr23> | 98 |
| 3 | <forr24> | <forr25> | <forr26> | 99 |
| 4 | <forr27> | <forr28> | <forr29> | 98 |
| 5 | <forr30> | <forr31> | <forr32> | 90 |
| 6 | <forr33> | <forr34> | <forr35> | 96 |

| | | | | |
|---|---|---|---|---|
| 7 | <forr36> | <forr37> | <forr38> | 93 |
| 8 | <forr39> | | <forr40> | 87 |
| 9 | <forr41> | <forr42> | <forr43> | 58 (>99^% ee) |
| 10 | <forr44> | <forr45> | <forr46> | 63 |
| 11 | <forr47> | <forr48> | <forr49> | 52 |
| 12 | <forr50> | <forr51> | - | 0 |
| 13 | <forr52> | <forr53> | - | 0 |

[a] Isolated yields of amide products for reactions conducted on 1.0^^mmol scale of alcohol (1.0^^equiv), amine (1.1^^equiv), [Ru] (1.0^^mol%) in toluene (2^^M), at 120^°C during 15^^h.

Table^^4 Hydrogenation of polar bonds catalyzed by complex **3**.<W=3>

<forr54>

| Entry | Substrate | Product | Yield [%][a] |
|---|---|---|---|
| 1 | <forr55> | <forr56> | 80[b] |
| 2 | HCOOMe | $CH_3OH$ | 14[c] |
| 3 | HCOOMe | $CH_3OH$ | 50 |

| | | | |
|---|---|---|---|
| 4 | <forr57> | <forr58> | 67[d] |
| 5 | PhCOOMe | BnOH, MeOH | 61[b,e] |
| 6 | $PhCOONH_2$ | - | 0[d] |
| 7 | <forr59> | - | 0[d] |
| 8 | <forr60> | <forr61> +MeOH | >99[f] |
| 9 | <forr62> | <forr63>+<forr64> +EtOH | >99[f] |
| 10 | <forr65> | <forr66> | 52[f] |
| 11 | <forr67> | <forr68> +2 MeOH | >99[f] |
| 12 | <forr69> | <forr70> | >99[f] |

[a] General reaction conditions: Substrate (1.0^^equiv), **3** (0.05^^mol%) in toluene at 80^°C, 8^^bar $H_2$ during 18^^h. The given yields were determined by GC-FID, except for methyl formate, which was calculated by $^1$H NMR, [b] **3** (1^^mol%) in THF at 65^°C, 8^^bar $H_2$, overnight, [c] In THF at 65^°C, 8^^bar $H_2$, overnight, [d] **3** (1^^mol%), [e] Benzyl benzoate was detected in *ca*. 7^%, [f] **3** (0.5^^mol%).