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ARTICLE

Selective conversion of alcohols in water to carboxylic acids by *in situ* generated ruthenium *trans* dihydrido carbonyl PNP complexes

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Cite this: DOI: 10.1039/xoxxoooooox

Received 3rd June 2014,
Accepted XXXth June 2014

DOI: 10.1039/xoxxoooooox

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In this work, we present a mild method for direct conversion of primary alcohols into carboxylic acids with the use of water as oxygen source. Applying a ruthenium dihydrogen based dehydrogenation catalyst for this cause; we investigated the effect of water during the catalytic dehydrogenation process of alcohols. Using 1 mol% of catalyst we report up to high yields. Moreover, we isolated key intermediates which play most likely a role in the catalytic cycle. One of the intermediates is identified as a *trans* dihydrido carbonyl complex which is generated *in situ* in the catalytic process.

Introduction

Catalytic oxidation of alcohols is an essential industrial and natural process and leads to important intermediates or products such as aldehydes, ketones or carboxylic acids. Established methods usually demand strong and toxic oxidants such as chromium or manganese oxides along with many additives.[1-4] In some cases, the use of stoichiometric oxygen supplying reactants or even the presence of pure pressurized oxygen is required.[5] In terms of the synthesis of carboxylic acids, mostly the oxidation of aldehydes as intermediates or starting materials is needed.[6] The methods of direct oxidation of alcohols into carboxylic acids are still behind and do not meet today's requirements of a clean and efficient pathway without the necessity of aggressive and toxic oxidants and by avoiding chemical waste products. Despite these disadvantages, only a small number of direct alcohol conversion into carboxylic acids were reported.[7] For example *Stark* et al. reported a direct oxidation method of alcohols involving tetra-n-proplyamonium perruthenate (TPAP) in the presence of N-methylmorpholine N-oxide (NMO) as a key additive to stabilise the aldehyde hydrate intermediate.[8] A different way was obtained by the *Grützmacher* group; they reported a homogenous catalytic transformation of alcohols to acids with high yields and under very mild conditions applying a rhodium based catalyst with cyclohexanone as hydrogen acceptor.[9, 10] With this similar concept they also accomplished to convert alcohols into esters or amides. The latest method was reported by the *Milstein* group in 2013 by applying a bipyridine based PNN ruthenium carbonyl hydride catalyst **1** using only water as oxygen source with no further additives (Figure 1).[11] Usually those pincer typed ruthenium complexes bearing cooperative (and hemi-labile) pincer-backbones are known for dehydrogenative coupling of alcohols into esters and their reverse hydrogenation reactions into alcohols, also for N-alkylation reactions from alcohols and amines.[12-15] In the presence of water, catalyst **1** is highly active for catalytic conversion of different alcohols into their corresponding carboxylic acid salts.

Other works about alcohol dehydrogenation in aqueous solution at low temperature, in particular methanol[16-18] and methanediol,[19] also showed the possibility of acceptorless dehydrogenation. In these certain cases the dehydrogenation resulted in the formation of carbon dioxide and hydrogen gas.

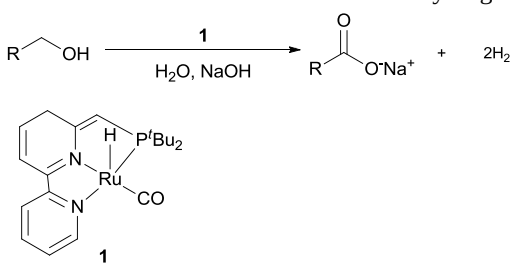

Figure 1 Direct oxidation of alcohols using a bipyridine ruthenium catalyst **1**.[11]

Inspired by the latest achievements, we present a setup using a ruthenium PNP pincer complexes [Ru(H_2)H_2(Me-PNP)] **2**[20] and [RuH_2(CO)(Me-PNP)] **3** for catalytic dehydrogenation of primary alcohols in the presence of water, respectively in absence of any other oxidants (Figure 2). Our reactions were

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conducted with aq. NaOH solution as the only additive to obtain the carboxylic acid salts in up to high yields. Furthermore, we isolated complex intermediates **3** and **4a-b** separately and from the catalytic process (Figure 2). In our system, complex **2** serves as precursor which converts *in situ* via alcohol decarbonylation reaction to a *trans* dihydrido complex [RuH_2(CO)(Me-PNP)] **3**. Separately, complex **3** was used for catalytic alcohol dehydrogenation reactions in water. Based on achievements in earlier reports, [12, 13, 21-25] we investigated the decarbonylation behaviour of similar PNP pincer based ruthenium complex [Ru(H_2)H(PNP)] **5**. Complex **5** can be transformed into a carbonyl complex [RuH(CO)(PNP)] **6** and converted into a *trans* dihydride complex [RuH_2(CO)(H-PNP)] **7** in hydrogen atmosphere (Figure 2). Those complexes are important intermediates for different transformations reported by others.[26, 27]

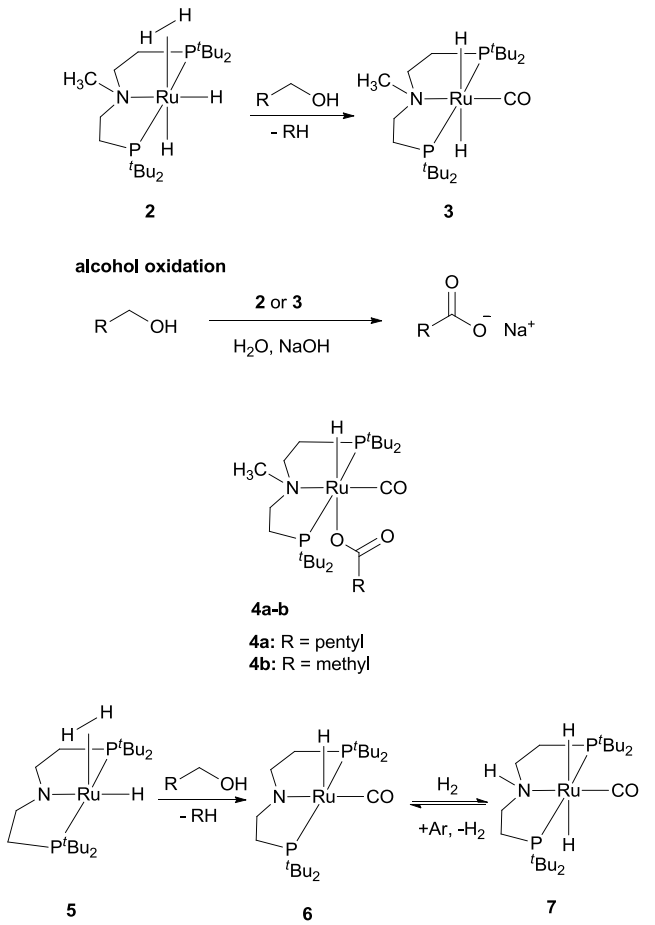

Figure 2 Ruthenium hydride [Ru(H_2)H_2(Me-PNP)] **2** and *trans* dihydrido carbonyl complex [RuH_2(CO)(Me-PNP)] **3** for alcohol oxidation, complex intermediates **4a-b**, [Ru(H_2)H(PNP)] **5** and carbonyl complexes [RuH(CO)(PNP)] **6** and RuH_2(CO)(H-PNP)] **7**.

Results and Discussion

Catalytic oxidation of alcohols

For standard catalytic procedure, a mixture of 2 ml water, 5 mmol of alcohol, 5.5 mmol of NaOH and 1.0 mol% of [Ru(H_2)H_2(Me-PNP)] **2** or [RuH_2(CO)(Me-PNP)] **3** was refluxed under continuous argon flow in an open system for 20 h at 120 °C. The addition of base (NaOH) is necessary to obtain the carboxylic acid salt and to shift the reaction equilibrium towards the product. After the reaction time, the predominant single aqueous phase was treated with diethyl ether to extract the catalyst. The aqueous layer was then acidified to convert the carboxylic acid salt into its corresponding carboxylic acid which was subsequently extracted with ethyl acetate. Isolated yields of the carboxylic acids are presented in Table 1. In this catalytic oxidation of alcohols we tested a series of aliphatic alcohols along with benzyl alcohol. Best results using catalyst **2** were obtained with hexanol and pentanol yielding 88 and 71% (entry 1 and 2), while butanol gave a moderate yield of 63% (entry 3). Catalysing longer aliphatic chained alcohols (entry 4 and 5), the isolated yields dropped down to 33%. This is probably due to a lack of miscibility of these less polar long-chain aliphatic alcohols with water. Benzyl alcohol and cyclohexyl methanol gave yields between 59 and 65% (entry 6 and 7). After the reaction and extracting the complex with diethyl ether, the organic phase contained only traces of unreacted alcohol, but no ester as by-product. A slight increase of the yields was obtained with complex **3**. The reaction of hexanol to hexanoic acid gave similar yields (entry 1 and 8), for butanol and pentanol (entry 9 and 10) an increase of around 10% were obtained. Isolated yields for octanol and decanol (entry 11-12) remained unchanged. The oxidation of benzyl alcohol to benzoic acid improved from 65% yield to 85% (entry 13). Contrary, the conversion of cyclohexyl methanol dropped to 36%. With complexes **5** and **6** the yields for the hexanol oxidation were 53% and 61% (Table 15 and 16).

Table 1 Dehydrogenation of alcohols in the presence of water.

Entry[a]	Cat.	Alcohol	Product	Yield
1	2	hexanol	hexanoic acid	88
2	2	pentanol	valeric acid	71
3	2	butanol	butyric acid	63
4	2	octanol	caprylic acid	42
5	2	decanol	decanoic acid	33
6	2	benzyl alcohol	benzoic acid	65
7	2	cyclohexyl methanol	cyclohexyl carboxylic acid	59
8	3	hexanol	hexanoic acid	92
9	3	pentanol	valeric acid	83
10	3	butanol	butyric acid	73
11	3	octanol	caprylic acid	45
12	3	decanol	decanoic acid	32
13	3	benzyl alcohol	benzoic acid	85
14	3	cyclohexyl methanol	cyclohexyl carboxylic acid	36
15	5	hexanol	hexanoic acid	53
16	6	hexanol	hexanoic acid	61

[a] reaction at 120 °C, 20 h with 1mol% cat. **2**, **3**, **5** or **6**, 5 mmol alcohol, 5.5 mmol NaOH.

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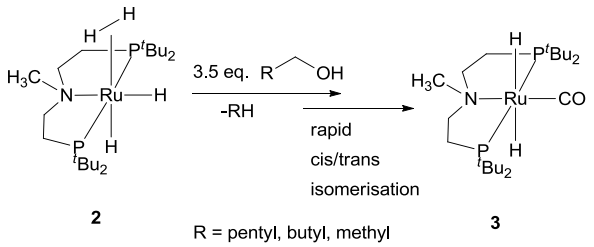
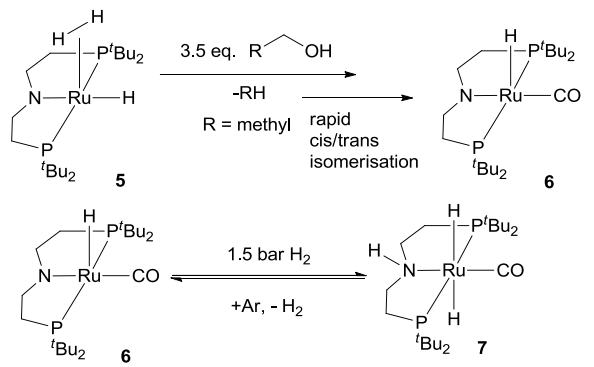
Formation of the active species and characterisation of the isolated complex intermediates

At the beginning of the catalysis, the *trans* dihydrido carbonyl complex [RuH_2(CO)(Me-PNP)] **3** is formed through decarbonylation of the primary alcohol by [$Ru(H_2)H_2$(Me-PNP)] **2** (Scheme 1). Separately in another experiment, complex **3** was obtained by adding 3.5 equivalents of ethyl, pentyl or hexyl alcohols to [$Ru(H_2)H_2$(Me-PNP)] **2** in a closed system at 80 °C for 48 h, with very good yields, which is stable under argon atmosphere at room temperature. Furthermore, a series of gas phase mass spectra were recorded to detect the fragmentations of the evolved aliphatic hydrocarbons from the decarbonylation reactions of the corresponding alcohols (supplementary information (SI) Fig. S1-2). The gas phase MS analysis clearly showed the formation of methane and butane from ethanol, respectively pentanol. Using deuterated ethanol with these hydride catalysts, we observed the formation of CD_3H confirming the interaction of the hydride-site with the substrate. Moreover, we confirmed the molar mass of complex **3** via LIFDI-MS technique (SI Fig. S3). Mechanistical investigations of decarbonylation reactions with ruthenium complexes were pioneered by *Kubas* and *Caulton*.[25] Following these observation and other indications,[28, 29] *Sabo-Etienne* et al. reported the decarbonylation reaction of alcohol by a molecular dihydrogen ruthenium complex, whereby, similar to our system, the dihydrogen ligand is replaced by a CO ligand.[22] Moreover, *Foxman* and *Ozerov* reported the CO functionalisation of a PNP typed ruthenium pincer hydride complex obtained through decarbonylation of acetone.[23] Based on previous reports by *Milstein* et al., we accordingly assume that a *cis*-[RuH_2(CO)(Me-PNP)] complex is generated in the first step, which undergoes then, despite the high *trans* influence of the hydride ligands, a rapid *cis-trans* isomerisation into the thermodynamically more stable and sterically more favourable *trans* isomer **3**.[28, 30-33] Furthermore, we observed no isomeric change in the ^{1}H- and ^{31}P{^{1}H}-NMR after heating complex **3** at 80 °C for 10 h. [RuH_2(CO)(Me-PNP)] **3** shows in the ^{1}H-NMR spectrum at 300 MHz a multiplet assigned to two hydrides at -5.40 ppm. At higher frequencies of 600 MHz, the multiplet resolves into two clean triplet signals at -5.43 ppm ($^2J_{HP}$ = *16.1 Hz*) and -5.54 ppm ($^2J_{HP}$ = *19.3 Hz*). Two signals for two hydride signals next to each other in the chemical shifts with a $^2J_{HP}$ coupling constant between 16-24 Hz is similar to other reported *trans* dihydride PNP pincer complexes with aliphatic backbones by *Gusev* and *Schneider*.[34-37] In the ^{13}C-NMR spectrum, the CO signal was found at 210.8 ppm (*t*, $^2J_{CP}$ = *13.2 Hz*), which was further confirmed by decarbonylation reactions of ^{13}C labeled ethanol (SI, Fig. S16). The *ν*CO band was detected at 1871 cm^{-1} while the comparing ^{13}CO band was found with a Δ43 at 1828 cm^{-1}. Vibration of the hydrides was found at 1642 cm^{-1} for complex **3** and 1640 cm^{-1} for the ^{13}C labeled complex (SI, Fig. S10). This is in agreement for the case of a typical *trans* dihydride arrangement. The CO stretching mode is located in the typical range with higher wave numbers followed by the M-H vibrations as one single, sharp band at lower wave numbers.[30, 32, 38] In contrary, for *cis* bonding modes of metal dihydrides, the hydride *trans* to a pincer backbone would have the highest wave number, followed then by the CO band and then with lowest wave number the hydride *trans* to the carbonyl ligand.[38]



Scheme 1 Decarbonylation of [$Ru(H_2)H_2$(Me-PNP)] **2** to [RuH_2(CO)(Me-PNP)] **3** via cis/trans isomerisation reaction.

Comparing the decarbonylation reactivity of **2**, similar observations were made from the reaction of the analogue ruthenium complex [$Ru(H_2)$H(PNP)] **5** which synthesis was reported in earlier works (Scheme 2).[20, 26] Decarbonylation reaction of ethanol by complex **5** gave the carbonyl complex [RuH(CO)(PNP)] **6** in excellent yields. In the ^{1}H-NMR spectrum, the hydride ligand gives a triplet signal in the upfield at -20.87 ppm ($^2J_{HP}$ = *16.3 Hz*), which indicates the configuration of the hydride ligand *cis* to the pincer ligand.[34] Experiments with ^{13}C labeled ethanol resulted with a triplet signal at 208.8 ppm ($^2J_{CP}$ = *10.5 Hz*) for the CO ligand in the $^{13}C_{APT}$-NMR spectrum. IR signals were found at 1872 cm^{-1} for the non labeled νCO vibration along with a weaker νRu-H band at 2052 cm^{-1} which are characteristic for pincer based carbonyl monohydride compounds.[30] For the ^{13}C labeled complex, the ^{13}CO band was detected at 1830 cm^{-1} and with a νRu-H vibration around 2062 cm^{-1} (Fig. S13). Pressurising complex **6** with 1.5 bar H_2 gas showed around 79% conversion of **6** into *trans* dihydride **7**, which exhibits, similar to complex **3**, two triplet signals at -5.86 ppm ($^2J_{HP}$ = *18.2 Hz*) and -6.13 ppm ($^2J_{HP}$ = *17.4 Hz*). Isolation of complex **7** was not possible due to the rapid degeneration into **6**.



Scheme 2 Decarbonylation of [$Ru(H_2)$H(PNP)] 5 to [RuH(CO)(PNP)] 6 via cis/trans isomerisation and the hydrogenation of 6 to [RuH_2(CO)(HPNP)] 7.

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Catalytic cycle and the isolation of intermediates 4a and b

Similar to the system reported by *Milstein et al.*, we assume that complex **3** dehydrogenates the alcohol into an aldehyde intermediate complex. It is also possible, that the aldehyde converts independently with water into an aldehyde hydrate intermediate. However, due to the rapid equilibrium between the aldehyde and the aldehyde hydrate intermediate,[11] it seems more plausible that the reaction with water under basic conditions generates an aldehyde hydrate, stabilised as a geminial diolate complex, which can be dehydrogenated into the carboxylate complex **4a** (Figure 3).[11] From there on, the carboxylate is salted out by sodium cation. In the presence of water, no formation of esters was observed since only unreacted alcohol residues were found in the reaction mixture after the appropriate reaction time. This observation confirms yet again that water suppresses the formation of ester.[11] Compared to previous studies[11] it is unclear if the mechanism involves a metal-ligand cooperativity during the catalytic reaction. We achieved the conversion of alcohols to carboxylic acids using catalysts **2** and **3** bearing a "non-cooperative" Me-PNP-ligand. The experimental data show that a basic position as proton acceptor/donor is not crucial for this reaction as no H/D exchange has been observed in the ligand backbone. The lack of H/D exchange in the ligand backbone let us tentatively exclude cooperative effects of the ligand. It is likely that the acceptorless dehydrogenation and oxygen-transfer from water solely takes place at the ruthenium core.

The attempt to isolate the complex intermediate species after the reaction time led to the isolation of **4a** which was extracted with toluene. Separate attempts led also to the isolation of **4a** either by refluxing complex **2** in hexyl alcohol and water or by the reaction of **3** with hexanoic acid (Figure 3). For the latter one, **4a** was obtained in very good yields within minutes under hydrogen evolution. Analogue, complex **4b** was obtained by adding acetic acid to complex **3** (Figure 3).

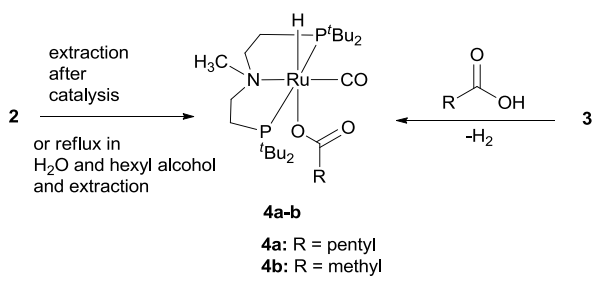

Figure 3 Isolation of complex **4a** and **4b**. Complex **4a** were obtained by extraction with toluene after the catalytic reaction with **2** or by refluxing **2** with hexyl alcohol in water. Adding acetic or hexanoic acid to complex **3** led directly to **4a** and **4b**.

Both complexes almost do not differ in their chemical shifts in the $^{31}P\{^{1}H\}$ NMR showing singlets around 81.4 ppm (complex **4a**) and 81.3 (complex **4b**), while exhibiting triplet signals in the upfield at -17.08 ppm ($^{2}J_{PH}$ = *20.7 Hz*, complex **4a**) and at -17.49 ppm ($^{2}J_{PH}$ = *20.4 Hz*, complex **4b**). IR spectra show the νCO for both complexes at 1908 cm^{-1}, while exhibiting the νC=O band at 1593 cm^{-1} (SI, Fig. S11-12). LIFDI-MS/MS analysis of complex **4a** showed only a fragmentation with the mass value of 506 m/z, which can be explained by the loss of the hexanoate under MS conditions, showing only the carbonyl monohydride species (for more details see SI, Fig. S5-6). This observation is in full agreement with our recent experiments applying LIFDI-MS analysis on ruthenium pincer hydrides complexes.[20] During a soft ionisation process, a mixture of similar fragmentations can be detected with this kind of compound class, which can be explained by the loss of the hydride ligands (-Δ1-2 m/z) causing a shift towards lower mass values.[20] In contrast to **4a**, LIFDI-MS/MS analysis of **4b** revealed the molar mass of 565 m/z which is in good agreement with the simulated isotope pattern (in red) illustrated in Figure 4. Compared to the simulated isotope pattern of [RuH(CO)(OOCCH$_3$)(Me-PNP)] 565 m/z in red, the LIFDI-MS/MS pattern is slightly shifted towards lower mass value, which can be explained by the detection of a fragmentation of the subspecies [Ru(CO)(OOCCH$_3$)(Me-PNP)] 564 which is generated during the ionisation process.

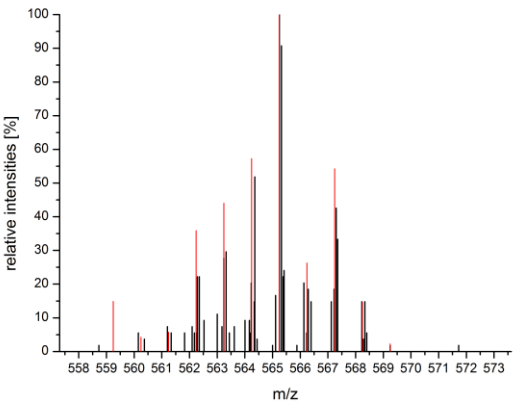

Figure 4. LIFDI-MS/MS analysis of [RuH(CO)(OOCCH$_3$)(Me-PNP)] 565 **4b** in toluene. Isotope pattern area 558-570 (black) in comparison to the simulated isotope pattern of [RuH(CO)(OOCCH$_3$)(Me-PNP)] 565 (red).

A single crystal structure of **4b** was obtained from crystals grown as red prism in a mixture of benzene and heptane at room temperature (Figure 5, selected bond distances and angles are given in Table 2). The structure shows a distorted octahedral coordination of the ruthenium core, where both locations of the P-atoms of the P-Ru-P axis are twisted out-of-plane with a P1-Ru-P2 angle of 157.24°. Same applies for the *trans*-arrangement of the hydride and the carboxylate with an angle of 169.20° (H1-Ru-O2). The x-ray pattern allowed the localisation of the hydride H1 giving a Ru-H distance of 1.57(4) Å. Furthermore, the *trans* arrangement of the CO ligand to the PNP-ligand is confirmed, which was discussed earlier in this work. The N-Ru-CO angle is closer to 180° (176.16°), consequently the H1-Ru-CO angle is near orthogonal (92.20°).

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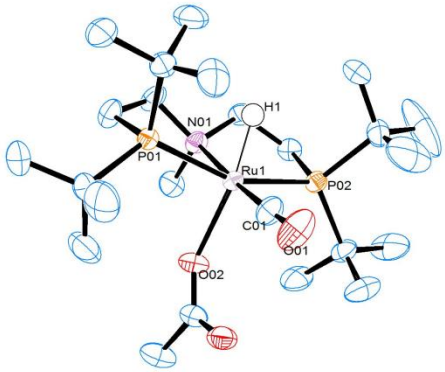

Figure 5. ORTEP diagram of the single crystal structure of complex **4b**. Ellipsoids are illustrated at 50% possibility. All hydrogen atoms not depicted here except for H1 for clarity.

Table 2. Selected bond distances[a] and angles[b] of complex **4b**.

Ru1-P1	2.34(9)	P1-Ru1-P2	157.24
Ru1-P2	2.34(6)	N01-Ru1-C01	176.16
Ru1-C01	1.82(0)	H1-Ru1-O02	169.30
Ru1-O02	2.21(9)	H1-Ru1-C01	92.20
Ru1-H1	1.57(4)		
Ru1-N01	2.24(7)		

[a] Distances are given in Å. [b] Angles are reported in degrees.

Conclusions

In summary of this work, we presented an approach for catalytic dehydrogenation of primary alcohols in water yielding carboxylic acid salts using ruthenium hydride complexes. Moreover, we confirmed that complexes **2** and **5** convert *in situ* into carbonyl *trans* dihydrides complexes **3** and **6** by decarbonylation reaction of alcohols. Complex intermediate **4a**, which was isolated after the catalysis as well as synthesised in different ways, is believed to be one of the complex species taking part in the catalytic cycle.

Experimental Section

Reactions were generally prepared under argon atmosphere using *Schlenk* techniques, flame-dried glassware and a *Labmaster 200* glove-box from *MBraun*. High-pressure hydrogen reactions were performed in a *Büchi Tinyclave* (50 mL) glass autoclave. All solvents and reagents were purchased from *Acros*, *Merck*, *Sigma-Aldrich*, *Fluka*, *Strem* or were acquired from the institute stock. Commercial anhydrous solvents and argon-as packed reagents were used as received and stored in the glove-box under argon. Non-anhydrous solvents were dried and distilled (under vacuum or argon) prior to use, applying standard procedures.

Analytic methods

^{1}H-, ^{13}C-, ^{31}P-NMR spectra were recorded at 300 MHz (^{1}H), 75 MHz (^{13}C) and 121 MHz (^{31}P) on a *Bruker Avance II 300* and on a *Bruker Avance II+ 600* spectrometer at 600 MHz (^{1}H), 150 MHz (^{13}C) and 242 MHz (^{31}P) using deuterated benzene and toluene at room temperature. ^{1}H shifts were reported in ppm (δ_H) downfield from TMS and were determined by reference to the residual solvent peaks (C_6D_6: 7.16 ppm, C_7D_8: 7.09 ppm.). Chemical shifts were reported as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). Coupling constants *J* were reported in [Hz]. For hydrogenation experiments, Young-Teflon Capped NMR tubes from *Wilmad* were used. Infrared spectra (IR) were measured at room temperature with a *Bruker Alpha* spectrometer equipped with a Diamond-ATR IR unit. Data are reported as follows: absorption $\tilde{\nu}$ [cm^{-1}], weak (w), medium (m), strong (s). Mass-spectrometric investigations of the gas composition in the gas phase were conducted with a HPR-20 gas analysis system by *Hiden Analytical* and were directly connected to the reaction set up under argon atmosphere. The HPR-20 QIC (*Hiden Analytical*) has a MS detection limit <0.09 ppm as xenon in air is detectable. Note the MS has sensitivity down to partial pressures of 10-^{10} torr (Note: spectrometer specific unit is torr not MPa).

General catalytic procedure

For standard catalytic procedure, 0.05 mmol of complex **2** or complex **3** were added to 5.5 mmol NaOH and 5 mmol of alcohol. After the addition of 2 mL degassed water, the content was refluxed at 120 °C for 20 h under constant argon flow in an open system. After the reaction time, the aqueous phase was extracted with diethyl ether to extract the catalyst and alcohol residues. The aqueous layer was then acidified with 20% aq. HCl and treated five times with 20 mL ethyl acetate. After the organic layers were combined and dried 1 h over $MgSO_4$, the solution was filtered and the solvent was removed in reduced pressure to obtain the isolated carboxylic acid. Yields are given in Table 1.

Synthesis of [RuH$_2$(CO)(Me-PNP)] 3

In an argon flushed *Büchi* glass autoclave 100 mg (0.198 mmol) of [Ru(H$_2$)H$_2$(Me-PNP)] **2** were dissolved in 6 mL toluene. The synthesis of complex **2** is described in our previous report.[20] After the addition of 3.5 eq. (0.693 mmol) of a primary alcohol (e.g. ethyl, pentyl, hexyl alcohol), the content was heated at 80 °C for 48 h. After the appropriate time, the solvent was removed in *vacuo* and the residue was washed twice with pentane. The grey powder was stored at -34 °C. Yield: 80%.

LIFDI-MS (argon collided): m/z 511.3 (2), 510.3 (19), 509.3 (55), 508.3 (33), 507.3 (100), 506.3 (73), 505.3 (74), 504.3 (65), 503.3 (30), 502.3 (17), 501.3 (22).

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^{1}H-NMR: (600 MHz, benzene-d_6): δ_H [ppm] = 2.32 (m, 2H, CH_2), 2.11 (s, 3H, NCH_3), 1.93 (m, 2H NCH_2), 1.61 (m, 2H, PCH_2), 1.55 – 1.52 (m, 2H, overlapped, PCH_2), 1.50 (dt, 36H, $^3J_{PH}$ = *6.7 Hz*, PC(CH_3)$_3$), -5.43 (t, 1H, $^2J_{PH}$ = *16.1 Hz*, Ru-H), -5.54 (t, 1H, $^2J_{PH}$ = *19.4 Hz*, Ru-H).
$^{13}C_{APT}$-NMR: (75 MHz, benzene-d_6): δ_C [ppm] = 210.8 ppm (*t*, $^2J_{CP}$ = *13.2 Hz*, *C*O, data extracted from ^{13}CO labled probe), 65.8 (t, $^2J_{CP}$ = 5.1 Hz, NCH_2), 52.9 (NCH_3), 36.4 (t, $^1J_{CP}$ = 8.9 Hz, P(*C*(CH_3)$_3$)), 33.9 (t, $^1J_{CP}$ = 7.4 Hz, P(*C*(CH_3)$_3$)), 30.3 (t, $^2J_{CP}$ = 3.3 Hz, P(C(*CH*$_3$)$_3$), 30.1 (t, $^2J_{CP}$ = 2.9 Hz, P(C(*CH*$_3$)$_3$)), 24.4 (t, $^1J_{CP}$ = 5.3 Hz, P*C*H$_2$).
^{31}P{^{1}H}-NMR: (121 MHz, benzene-d_6): δ_P [ppm] = 106.3 (s).
IR: $\tilde{\nu}$[cm^{-1}]=2950 - 2864 (m), 1871 (s), 1640 (s), 1474 (m), 1458 (m), 1416 (w), 1383 (m), 1381 (m), 1351 (m), 1310 (w), 1208 (w), 1171 (m), 1049 (w), 1025 (m), 930 (w), 915 (w), 881 (m), 801 (m), 739 (m), 679 (m), 644 (w), 613 (m), 566 (m), 529 (w), 508 (w), 478 (m), 432 (m).

Isolation of [RuH(CO)(hexanolate)(Me-PNP)] **4a**

In an argon flushed *Schlenk flask* equipped with a bubbler, 50 mg (0.1 mmol) of [RuH$_2$(CO)(Me-PNP)] **3** were dissolved in 5 mL toluene. After the addition of 1.5 eq. (0.15 mmol) hexanoic acid, the content was stirred for 30 min under a constant stream of argon. The solvent was removed in *vacuo* and the product was washed twice with pentane. The grey powder, yielding 85%, was stored at -34 °C.
LIFDI-MS/MS (fragment 506): m/z 509.3 (13.1), 508.3 (33.3), 507.3 (16.7), 507.2 (9.5), 506.3 (100), 505.3 (97.6), 504.3 (47.6), 503.3 (16.7), 502.2 (16.7), 501.1 (4.8), 500.2 (9.5).
^{1}H-NMR: (600 MHz, benzene-d_6): δ_H [ppm] = 2.51 (t, 2H, $^2J_{CH}$ = 7.6 Hz, OOC*CH*$_2$(CH_2)$_3$$CH_3$), 2.17 (s, 3H, NCH_3), 2.14 (m, 4H, NCH_2), 1.70 (m, 2H, OOCCH$_2$*CH*$_2$(CH_2)$_2$$CH_3$), 1.55 – 1.51 (m, 8H, overlapped, 4H PCH_2 and 4H OOC(CH_2)$_2$(*CH*$_2$)$_2$$CH_3$), 1.38 (t, 18H, $^3J_{PH}$ = 6.5 Hz, P(C(*CH*$_3$)$_3$), 1.23 (t, 18H, $^3J_{PH}$ = 6.1 Hz, P(C(*CH*$_3$)$_3$), 0.99 (t, 3H, $^2J_{CH}$ = 7.3 Hz, OOC(CH_2)$_4$*CH*$_3$), -17.08 (t, 1H, $^2J_{PH}$ = 20.7 Hz, Ru-H).
$^{13}C_{DeptQ}$-NMR: (150 MHz, benzene-d_6): δ_C [ppm] = 208.5 ppm (s, *C*O), 175.8 (s, CH_3*C*OO), 65.8 (s, NCH_2), 45.6 (s, NCH_3), 40.8 (s, OOC*C*H$_2$(CH_2)$_3$$CH_3$), 37.5 (t, $^1J_{PC}$ = *5.1 Hz*, P(*C*(CH_3)$_3$)), 36.8 (t, $^1J_{PC}$ = *10.3 Hz*, P(*C*(CH_3)$_3$)), 33.0 (s, OOCCH$_2$*C*H$_2$(CH_2)$_2$$CH_3$), 30.6 (s, P(C(*CH*$_3$)$_3$), 30.5 (s, P(C(*CH*$_3$)$_3$)), 27.2 (s, OOC($CH_2$)$_2$*C*H$_2$$CH_2$$CH_3$), 23.7 (s, OOC($CH_2$)$_3$*C*H$_2$$CH_3$), 23.4 (s, P*C*H$_2$), 14.2 (s, OOC($CH_2$)$_4$*C*H$_3$).
^{31}P{^{1}H}-NMR: (121 MHz, benzene-d_6): δ_P [ppm] = 81.4 (s).
IR: $\tilde{\nu}$[cm^{-1}]=2959 - 2868 (m), 2126 - 2075 (w), 1908 (s), 1595 (s), 1466 (m), 1429 (w), 1389 (m), 1369 (m), 1354 (m), 1175 (m), 1043 (m), 1024 (m), 958 (w), 933 (w), 907 (w), 879 (m), 828 (w), 807 (m), 736 (m), 680 (m), 643 (m), 609 (m), 570 (m), 546 (m), 531 (m).

Isolation of [RuH(CO)(OOCCH$_3$)(Me-PNP)] 4b

In an argon flushed *Schlenk flask* equipped with a bubbler, 30 mg (0.06 mmol) of [RuH$_2$(CO)(Me-PNP)] **3** were dissolved in 5 mL toluene. After the addition of 1.5 eq. (0.09 mmol) acetic acid, the content was stirred for 30 min under a constant stream of argon. The solvent was removed in *vacuo* and the product was washed twice with pentane. The grey powder, yielding 81%, was stored at -34 °C.
LIFDI-MS/MS: m/z 569.2 (1.9), 568.2 (14.8), 567.3 (42.6), 566.3 (18.5), 565.3 (100), 564.4 (51.9), 563.2 (27.8), 561.2 (7.4), 560.2 (5.6).
^{1}H-NMR: (600 MHz, benzene-d_6): δ_H [ppm] = 2.22 (s, 3H, OOC*CH*$_3$), 2.13 (m, 4H, NCH_2), 2.09 (s, 3H, NCH_3), 1.63 (m, 2H PCH_2), 1.49 (m, 2H, PCH_2), 1.31 (t, 18H, $^3J_{PH}$ = *6.4 Hz*, P(C(*CH*$_3$)$_3$), 1.18 (t, 18H, $^3J_{PH}$ = *6.2 Hz*, P(C(*CH*$_3$)$_3$),-17.49 (t, 1H, $^2J_{PH}$ = *20.4 Hz*, Ru-H).
$^{13}C_{DeptQ}$-NMR: (150 MHz, benzene-d_6): δ_C [ppm] = 208.8 ppm (s, *C*O), 175.4 (s, CH_3*C*OO), 65.7 (s, NCH_2), 45.2 (s, NCH_3), 37.2 (t, $^1J_{CP}$ = *5.3 Hz*, P(*C*(CH_3)$_3$)), 36.7 (t, $^1J_{CP}$ = *10.2 Hz*, P(*C*(CH_3)$_3$)), 30.5 (s, P(C(*CH*$_3$)$_3$), 30.2 (s, P(C(*CH*$_3$)$_3$)), 23.6 (s, P*C*H$_2$).
^{31}P{^{1}H}-NMR: (242 MHz, benzene-d_6): δ_P [ppm] = 81.3 (s).
IR: $\tilde{\nu}$[cm^{-1}]=2956 - 2859 (m), 2145 - 2059 (w), 1906 (s), 1593 (s), 1464 (m), 1389 (m), 1368 (m), 1354 (m), 1259 (s), 1175 (m), 1087 (s), 1021 (s), 934 (w), 907 (w), 878 (m), 800 (s), 735 (m), 680 (m), 609 (m), 569 (m), 546 (w), 529 (w), 478 (m).

Synthesis of [RuH(CO)(PNP)] 6

In an argon flushed *Büchi* glass autoclave 100 mg (0.215 mmol) of [Ru(H$_2$)H(PNP)] **5** were dissolved in 6 mL toluene. The synthesis of complex **5** is described in our previous report.[20] After the addition of 3.5 eq. (0.753 mmol) of a primary alcohol (e.g. ethyl, pentyl, hexyl alcohol), the content was heated at 80 °C for 48 h. After the appropriate time, the solvent was removed in *vacuo* and the residue was washed twice with pentane. The orange powder was stored at -34 °C. Yield: 90%.
LIFDI-MS/MS: m/z 495.1 (1.0), 494.3 (15.9), 493.3 (46.1), 492.3 (14.6), 491.3 (100), 490.2 (34.7), 489.2 (39.6), 488.3 (28.9), 487.3 (4.6), 486.2 (2.4), 485.3 (15.5).
^{1}H-NMR: (300 MHz, benzene-d_6): δ_H [ppm] = 3.49 (m, 2H, CH_2), 3.14 (m, 2H, CH_2), 1.88 (m, 4H, PCH_2), 1.26 (dt, 36H, $^2J_{PH}$ = 14.3 Hz, PC(*CH*$_3$)$_3$), -20.87 (t, 1H, $^2J_{PH}$ = 16.3 Hz, Ru-H).
$^{13}C_{APT}$-NMR: (75 MHz, benzene-d_6): δ_C [ppm] = 208.8 ppm (*t*, *C*O, $^2J_{CP}$ = *10.5 Hz*, data extracted from ^{13}CO labeled probe in toluene-d_8), 63.5 (t, $^2J_{CP}$ = 7.1 Hz, NCH_2), 35.4 (t, $^1J_{CP}$ = 7.7 Hz, P(*C*(CH_3)$_3$)), 33.9 (t, $^1J_{CP}$ = 7.4 Hz, P(*C*(CH_3)$_3$)), 29.7 (t, $^2J_{CP}$ = 3.0 Hz, P(C(*CH*$_3$)$_3$), 28.5 (t, $^2J_{CP}$ = 3.2 Hz, P(C(*CH*$_3$)$_3$)), 26.0 (t, $^1J_{CP}$ = 6.9 Hz, P*C*H$_2$).
^{31}P{^{1}H}-NMR: (121 MHz, benzene-d_6): δ_P [ppm] = 110.1 (s).
IR: $\tilde{\nu}$[cm^{-1}]=2943 - 2800 (m), 2706 (w), 2628 (w), 2068 - 2048 (m), 1869 (s),
1469 (m), 1454 (m), 1385 (m), 1358 (m), 1318 (w), 1262 (m), 1206 (m), 1178 (m), 1157 (w), 1106 (w), 1063 (m), 1017 (m), 967 (m), 936 (w), 806 (s), 773 (w), 729 (s), 695 (m), 674 (w), 611 (m), 579 (m), 536 (m), 471 (s).

Hydrogenation of [RuH(CO)(PNP)] 6 to [RuH$_2$(CO)(HPNP)] 7

In a Young-Teflon capped NMR tube 7 mg (0.014 mmol) [RuH(CO)(PNP)] **6** were dissolved in 0.5 mL deuterated

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benzene. The content was pressurised with 1.5 bar H_2 gas. After 10 h, 79% conversion was detected via $^{31}P\{^1H\}$-NMR. Only hydride signals are clearly visible.
^{1}H-NMR: (300 MHz, benzene-d_6): δ_H [ppm] = -5.86 (t, 1H, $^2J_{PH}$ = 18.2 Hz, Ru-H), -6.13 (t, 1H, $^2J_{PH}$ = 17.4 Hz, Ru-H).
$^{31}P\{^1H\}$-NMR: (121 MHz, benzene-d_6): δ_P [ppm] = 110.1 (s, 21%, complex **6**), 108.9 (s, 79%, complex **7**).

Acknowledgements

We acknowledge the Ministerium für Innovation, Wissenschaft und Forschung NRW (MIWF-NRW) for financial support within the Energy Research Program for the Scientist Returnee Award for M. H. G. Prechtl (NRW-Rückkehrerprogramm). For access to LIFDI-MS analysis, we gratefully acknowledge Prof. Dr. T. Braun (Humboldt-University of Berlin, Germany). J-H. Choi wants to thank Dr. J. Neudörfl, T. Heidemann and A. Krest for helpful discussion. P. Kliesen is acknowledged for technical support for the XRD measurement.

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† † Electronic Supplementary Information (ESI) available: DOI: 10.1039/b000000x/
‡ For experimental section, limited spectral and crystallographic data see ESI.

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ABSTRACT

Selective conversion of alcohols in water to carboxylic acids by *in situ* generated ruthenium *trans* dihydrido carbonyl PNP complexes

Cite this: DOI: 10.1039/xoxxoooooox

Received 2nd June 2014,
Accepted XXXth June 2014

DOI: 10.1039/xoxxoooooox

www.rsc.org/

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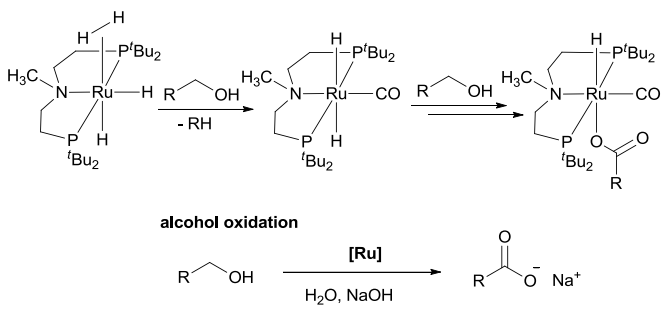
In this work, we present a mild method for direct conversion of primary alcohols into carboxylic acids with the use of water as oxygen source. Applying a ruthenium dihydrogen based dehydrogenation catalyst for this cause; we investigated the effect of water during the catalytic dehydrogenation process of alcohols. Using 1 mol% of catalyst we report up to high yields. Moreover, we isolated key intermediates which play most likely a role in the catalytic cycle. One of the intermediates is identified as a *trans* dihydrido carbonyl complex which is generated *in situ* in the catalytic process.



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† † Electronic Supplementary Information (ESI) available: DOI: 10.1039/b000000x/

‡ For experimental section, limited spectral and crystallographic data see ESI.

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