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Letter

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Catalytic Conversion of Alcohols to Carboxylic Acid Salts and Hydrogen with Alkaline Water

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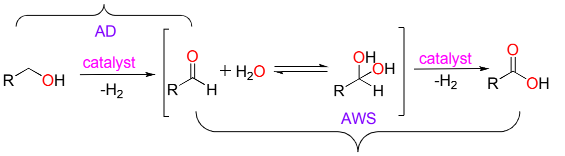
ABSTRACT: A $[RuH(CO)(py–NP)(PPh_3)_2]Cl$ (**1**) catalyst is found to be effective for catalytic transformation of primary alcohols, including amino alcohols, to the corresponding carboxylic acid salts and two molecules of hydrogen with alkaline water. The reaction proceeds *via* acceptorless dehydrogenation of alcohol, followed by a fast hydroxide/water attack to the metal-bound aldehyde. A pyridyl-type nitrogen in the ligand architecture appears to accelerate the reaction.

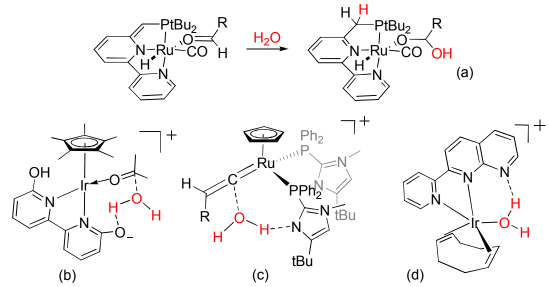
KEYWORDS: water addition, aldehyde–water shift, acceptorless dehydrogenation, carboxylic acids, naphthyridine

Carboxylic acids are an important class of organic compounds which serve as synthetic precursors for a wide array of value–added chemicals.[1] However, large–scale syntheses of carboxylic acids are still being carried out by oxidizing aldehydes with stoichiometric amount of oxidants such as permanganate, chromate, chlorite generating copious waste.[2] A few recent efforts are directed to realize an atom–economical, safe and environmentally benign method for metal–catalyzed transformation of alcohols to acids.[3] Grützmacher reported rhodium catalyzed dehydrogenative coupling of primary alcohols and water to acids using sacrificial ketones or alkenes as hydrogen acceptors.[4] Another version of this reaction used atmospheric O_2 as the oxidant and DMSO as the oxygen acceptor.[5] The real impetus towards oxidation of alcohols to acids was provided by Milstein's elegant Ru–PNN pincer complex which favored the reaction at low catalyst loadings and, most importantly, without the aid of hydrogen acceptors.[6a, 6b] Grützmacher and Beller independently studied dehydrogenation of methanol–water mixtures to hydrogen and carbon dioxide through the intermediacy of formic acid.[7]



Scheme 1. Alcohol Dehydrogenation (AD) followed by Aldehyde–Water Shift (AWS) Reaction

We took the following approach to design catalyst for dehydrogenative coupling of primary alcohols and water to acids. Direct conversion of alcohols to carboxylic acids can be considered as two consecutive reactions: 1. acceptorless dehydrogenation (AD) of alcohol to aldehyde, 2. subsequent 'aldehyde–water shift' (AWS)[8] reaction (Scheme 1). An '*ideal catalyst*' can be designed by assembling the necessary traits required to facilitate both reactions. Ru–hydrides are widely documented as intermediates in catalytic alcohol dehydrogenation.[9] Hence, $RuHCl(CO)(PPh_3)_3$– a commercially available and stable Ru–hydride was used as the core unit of the catalyst. Subsequently, we focused on the AWS reaction that involves water reacting with a metal–bound aldehyde. Several ligand systems have been devised for heterolytic splitting of water and subsequent hydroxide attack to the substrates.[10] Heterolytic splitting of water caused aromatization of the ligand skeleton for Milstein's catalyst (Scheme 2a).[6a,11] Gas phase calculations by Cundari, Goldberg and Heinekey revealed a simultaneous water proton migration to the anionic ligand and nucleophilic hydroxide attack to Ir–bound aldehyde (Scheme 2b).[8c,d] Grotjahn reported alkyne hydration catalysts where pendant basic groups in the ligand framework serve as an internal base to promote water attack to electrophilic vinylidene carbon (Scheme 2c).[12] We recently reported water activating ability of 2–(2–pyridyl)–1,8–naphthyridine (py–NP).[10a,13] Hydrogen bonding interaction of a free naphthyridine nitrogen with a metal–bound water promotes water addition to the metal leading to oxygenation of the Ir–bound 1,5–cyclooctadiene (Scheme 2d).[13] Ligand–assisted water dissociation was computed to be a favorable process than direct water oxidative addition to the metal center.



Scheme 2. Ligand–Assisted Water Reaction

With this background in mind, we sought to examine the efficacy of a catalytic system, arising out of the combination of py–NP and $RuHCl(CO)(PPh_3)_3$, for alcohol conversion to carboxylic acid with water. Herein, a non-pincer catalyst $[RuH(CO)(py–NP)(PPh_3)_2]Cl$ (**1**) is reported that is efficient towards dehydrogenative coupling of alcohols to the corresponding carboxylic acid salts and hydrogen with alkaline water. A pyridyl–type nitrogen in the ligand architecture polarizes the water molecule through hydrogen-bond interaction thus promoting AWS reaction.

Reaction of py–NP with $RuHCl(CO)(PPh_3)_3$ in THF gave **1** in 88% yield after 4 h at room temperature. The py–NP binds in a chelating mode with the pyridine nitrogen and one of the NP nitrogens (Figure 1). Ru1–H1A distance is 1.429(19) Å. Two *trans* PPh_3 ligands (Ru–P = 2.3497(6) Å) and a carbonyl (Ru1–C14 = 1.845(4) Å) complete the coordination sphere of the central ruthenium. A characteristic triplet at δ −9.01 ppm in ^1H NMR confirms the presence of a metal–hydride (See, Figure S1). The chemical equivalency of two phosphines is expressed as a single peak at δ 46.1 ppm in ^{31}P NMR (See, Figure S3). Solid state IR spectrum shows $\nu_{Ru–H}$ at 2005 cm^{-1} and ν_{CO} at 1915 cm^{-1}. The ESI–MS exhibits signal at *m/z* 862.169 (z = 1) attributed to $[\mathbf{1}–Cl]^+$ (See, Figure S6).

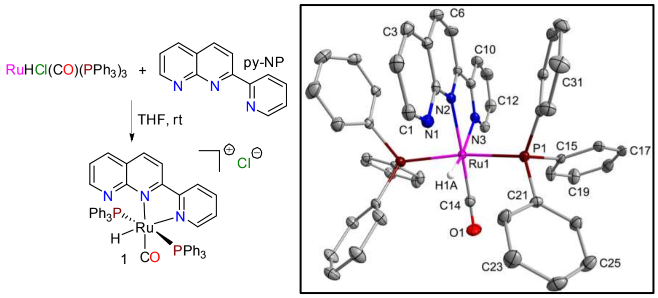


Figure 1. Synthesis of **1**. Molecular structure of the cationic unit in **1** is depicted inset.

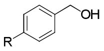
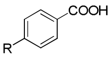
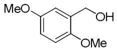
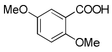
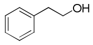
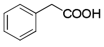
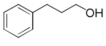
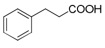
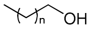
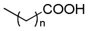
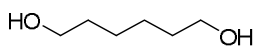
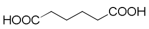
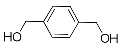
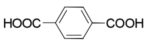
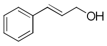
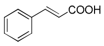
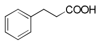
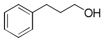
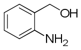
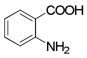
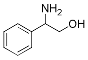
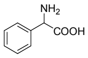
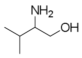
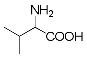
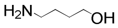
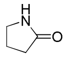
Complex **1** was evaluated as a catalyst for the conversion of primary alcohols to carboxylic acids with 5% catalyst loading at 110°C in presence of alkaline water under strict nitrogen atmosphere. The corresponding acid salts produced were neutralized with HCl and then extracted with EtOAc for further analyses. Lowering the temperature to 80°C had a detrimental effect on the acid conversion (See, entry 2, Table S2). Benzyl alcohol showed quantitative conversion to benzoic acid (Table 1, entry 1). The reaction was extended to electron rich aromatic alcohols and they showed excellent yields (entries 2, 3 and 6). The reaction was considerably slow for electron deficient aromatic alcohols (entries 4, 5). Both substrates, however, showed >95% yield when the reaction time was extended to 24 h. 2–Phenylethanol and 3–phenyl–1–propanol gave corresponding acids in high yields (entries 7, 8). The benzylic position was not compromised suggesting that a radical or rearrangement mechanism was not operative here. Under identical conditions, aliphatic alcohols showed lower conversions. So small amounts (0.1 mL) of 1,4 dioxane as a co–solvent were added to promote homogeneity for better efficiency. We obtained satisfactory results when the duration of the reaction was increased to 24 h (entries 10–12). When a diol was used, dicarboxylic acid was obtained as a major product (58%) with small quantities of lactone (12%) (entry 13). For terephthalic acid, dicarboxylic acid product was obtained exclusively (entry 14). Interestingly, when cinnamyl alcohol was used as a substrate (entry 15), apart from the expected acid product, reduced forms of the substrate and the acid were also obtained attributed to the generated H_2 gas (*vide infra*).[6a] Conventional synthesis of amino acids from amino alcohols usually require protection and deprotection steps of amine groups.[14] We attempted a direct, atom–economic and safe synthesis of amino acids using this dehydrogenation protocol.[6b] When 2–aminobenzyl alcohol was employed as starting material, corresponding anthranilic acid was obtained quantitatively (entry 16). 2–Phenylglycinol showed appreciable yields of amino acid (78%, entry 17). Aliphatic amino alcohols were considerably less reactive as seen for valinol (35%, entry 18). However, for 4–amino–1–butanol, cyclic γ–butyrolactam was obtained in 86% yield (entry 19).

Conversion of primary alcohol to carboxylic acid is accompanied by the concomitant release of two molecules of hydrogen. A volumetric analysis using gas buret revealed near-quantitative formation of two equivalents of hydrogen (See, Figure S17). The generated hydrogen gas was identified by GC (thermal detector) techniques (See, Figures S18–19). In another experiment, the catalytic reaction was conducted in a flask that was connected to a second flask in which equimolar styrene and a catalytic amount of $RhCl(PPh_3)_3$ in benzene were placed.[15] Ethylbenzene was detected in the second flask after the completion of the reaction demonstrating that hydrogen gas is generated in the reaction (See, Scheme S1). Evidently, the reaction is more efficient in an 'open system' where evolved hydrogen escapes from the reaction mixture and drives the reaction forward (See, entry 10, Table S2).

The homogeneous nature of the catalytic system was confirmed by mercury addition experiments.[16] Since a high pH was maintained throughout the reaction, other possible but less likely scenarios were also considered. A reaction with benzyl alcohol in absence of the catalyst was ineffective (See, entry 4, Table S2). When non–enolizable benzaldehyde was used under similar condition, only trace amount (<3%) of benzoic acid was obtained (See, entry 5, Table S2). A Cannizzaro disproportionation pathway is thus less likely to be the main route. Related Tischenko reaction would render ester as an intermediate susceptible to hydrolysis in alkaline media. However, no ester was detected under any circumstances when catalytic reactions were performed either in water or in organic solvents, and in presence and absence of base (See, entries 6–7, Table S2). These results discount the intermediacy of ester during acid synthesis.

Table 1. Conversion of Primary Alcohols to Carboxylic Acids with Alkaline Water Catalyzed by 1[a]

$$RCH_2OH + H_2O \xrightarrow{\mathbf{1},\ ^{-}OH} RCOO^{-} + 2\,H_2$$

Entry	Substrate	Product	Time (h)	Yield (%)[b]
1–5 R=H, Me, OMe, NO_2, F			6	100, 93, 100, 70, 62
6			6	100
7			6	100
8			6	98
9–12 n=2, 4, 6, 15			24	78, 76[c], 61[c], 59[c]
13			24	58[c] (+ 12% lactone)
14			24	95
15		  	24	75 (3:4:8)
16			24	99
17			24	78
18			24	35
19			24	86[d]

[a] Reaction conditions: 1 mmol alcohol, **1** (5 mol%), degassed, deionized alkaline water (18.5 mmol NaOH in 3 mL water), 110°C. [b] Carboxylic acids were obtained by acid treatment of the salts and determined by GC–MS using dodecane (1 mmol) as internal standard. [c] 0.1 mL dioxane added. [d] Yield determined by ^1H NMR.

Despite alkaline pH, no traces of aldol products were obtained for enolizable aldehydes. This suggests that the generated aldehyde is only a transient intermediate.[6a,7b] For an efficient AWS reaction, the generated aldehyde needs to be metal–bound when water adds to the carbonyl carbon. Introduction of one equivalent of pyridine as an additive impedes the product formation (See, entry 9, Table S2). A plausible rationalization is that pyridine binds to the metal and thus prohibits aldehyde coordination. Regardless, the only species detected throughout the catalysis were the acid products and the unreacted starting material.

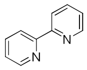
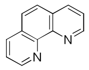
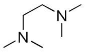
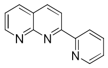
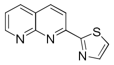
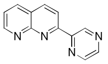
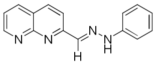
$^{18}OH_2$ (99%) mixed with known amounts of $Na^{16}OH$ and benzyl alcohol was stirred to give a mixture that was calculated to be ~60% ^{18}O labeled. Subsequent catalysis with 5 mol% **1** produced both ^{16}O and ^{18}O incorporated benzoic acids after 4h in the ratio 5:6 (~55% ^{18}O labeling) as revealed in GC–HRMS spectrum (See, Figure S20). A close agreement between the calculated and observed ^{18}O product shows that the source of incorporated oxygen atom in acid is water and not dioxygen.

Kinetic studies reveal that the reaction is 1.4±0.02 times slower for benzyl alcohol in D_2O than in H_2O indicating that O–H bond cleavage is not necessarily involved in the rate determining step (RDS) (See, Figure S21). A competition reaction between benzyl alcohol and benzyl alcohol–α,α–d_2 ($PhCD_2OH$) showed high KIE value of 5.2±0.04, suggesting that aldehyde generation might be one of the slower steps of the reaction (See, SI). This is also reflected in the long induction periods for the reaction followed by an enhancement in the rate of product formation (See, Table S3).

D–labeling experiments were carried out to examine the contribution of alcohol and water in the catalytic cycle. Use of either D-labeled alcohol, or water, or both would generate H_2, HD or D_2 gases during the reaction. The relative ratios of these evolved gases were estimated by monitoring the D-content in ethylbenzene while adding styrene in the reaction.[17] We performed three sets of reactions with $PhCH_2OH–D_2O$, $PhCD_2OH–H_2O$ and $PhCD_2OH–D_2O$. D–ethylbenzene was observed as the major product for the first two reactions (H_2: HD: D_2 = 1.5: 2.5: 1 and 3.1: 5.4: 1 respectively). However, for $PhCD_2OH–D_2O$, D_2–ethylbenzene was obtained as the major product (H_2: HD: D_2 ratio 1: 1.6: 2.5). D-labeling of both alcohol and water clearly affects the evolved gas composition from HD major to D_2 major signifying their contribution in the catalytic cycle (See, Figures S23, S24, Scheme S2). Although protic–hydridic exchange in alkaline media is substantial, the observed results clearly suggest the involvement of water in the reaction.

Control experiments were performed to investigate the influence of ligands towards the efficacy of the catalyst. $RuHCl(CO)(PPh_3)_3$, in absence of a ligand was ineffective under identical reaction conditions (Table 2, entry 2a). Several ligands were added to $RuHCl(CO)(PPh_3)_3$ and screened for the reaction. Ligands bpy, 1,10–phenanthroline, TMEDA which do not offer a nitrogen in the vicinity of the metal center, showed poor activity (<25% yield, entries 2b–2d). However, employing 2–substituted NP derivatives led to significantly higher yields of carboxylic acid products (82–99%, entries 2e–g). 2–((2–phenylhydrazono)methyl)–1,8–naphthyridine (phm–NP) was, however, less effective as a ligand (entry 2h) (*vide infra*). Molecular structures of complexes containing bpy (**2**) and phm–NP (**3**) ligands were also determined. (See, Figures S15, S16). Interestingly, doubling the NaOH amount under otherwise identical conditions led to an increase in yield to 65% for **2**. The positive role of the ligand is masked under increased hydroxide concentration.

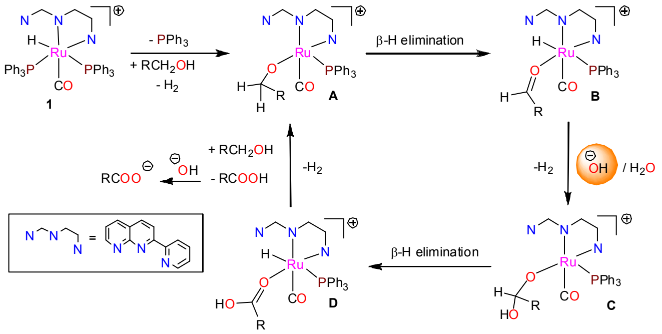
Table 2. Ligand Screening[a]

No ligand 2a, 0%	 2b, 25%	 2c, 20%	 2d, <10%
 2e, 99%	 2f, 85%	 2g, 82%	 2h, 38%

[a] Reaction conditions: 1 mmol benzyl alcohol, $RuHCl(CO)(PPh_3)_3$ (5 mol%), ligand (5 mol%), degassed, deionized alkaline water (18.5 mmol NaOH in 3mL water), 110°C. Yields were determined by GC–MS using dodecane (1 mmol) as internal standard after 6 h.

A tentative mechanism is proposed based on experimental findings (Scheme 3). Dissociation of one of the phosphine ligands from **1** is followed by alcohol coordination and the release of a hydrogen molecule in unison forming a Ru–alkoxide intermediate **A**.[18] An alkoxide attack to the central metal ion is a possibility in strong alkaline medium; however, in that case the solvent cage would be involved in the first hydrogen release (See, Scheme S3).[7b] The Ru–alkoxide intermediate then undergoes a β–H elimination to yield an aldehyde–bound Ru–hydride intermediate **B**. Because the free aldehyde is barely detected in solution, it is proposed that the aldehyde undergoes a series of fast reactions while still being coordinated to the metal. Since the reaction is carried out in alkaline medium, a direct attack of aqueous hydroxide to the aldehyde carbon is considered. Here again, solvent cage would facilitate the release of the second molecule of hydrogen. This assertion is in line with Beller's dehydrogenation mechanism of methanol/water mixture in alkaline medium.[7b] The Ru–gem–diolate intermediate **C** then undergoes a second β–H elimination to form **D** where acid is coordinated to the metal. The base present favors detachment of the acid species from the metal and thus drives the equilibrium towards acid salt formation.

The reaction does not proceed in non-aqueous medium. $^{18}OH_2$ and D-labeling studies suggest the direct involvement of water in the acid formation. Further, 2–substituted naphthyridine ligands, which offer a free nitrogen atom, display superior activity (Table 2). A plausible rationale is that the pyridyl–type nitrogen from naphthyridine unit enhances the nuleophilicity of a water molecule through hydrogen bonding interactions favoring aldehyde hydroxylation (See, Scheme S4a).[13] The unbound nitrogen can also promote a solvated hydroxide attack through hydrogen bonding with water molecule of the solvent cage (See, Scheme S4b). Alternatively, the unbound nitrogen may facilitate a hydroxide attack by coordination with Na$^+$.[19] Although the role of the naphthyridine based ligands in accelerating the reaction is evident, the exact mechanism of action is not clear.



Scheme 3. Proposed Catalytic Cycle for Alcohol to Acid Conversion in Alkaline Water

In conclusion, we report an efficient non-pincer catalyst for the dehydrogenative coupling of alcohols to the corresponding carboxylic acid salts using alkaline water. Mechanistic studies point to an initial acceptorless alcohol dehydrogenation followed by the fast attack of hydroxide/water to the metal-coordinated aldehyde. The precise role of 2–substituted naphthyridine ligands in accelerating the reaction is currently being investigated.

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Notes

The authors declare no competing financial interests.

ASSOCIATED CONTENT

Details of synthesis, X-ray data, catalytic experiments, cross-over experiments are provided in the SI. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Catalyst **1** hydrogenates styrene quantitatively (See, SI). Therefore, styrene was directly added in the reaction mixture and ethylbenzene was observed albeit in lower yields.

(18) Drastic reduction in benzoic acid yield was observed when the reaction was carried out in presence of excess PPh_3, suggesting PPh_3 dissociation from **1** in the initial step (See, Figure S22).

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Table of Contents artwork