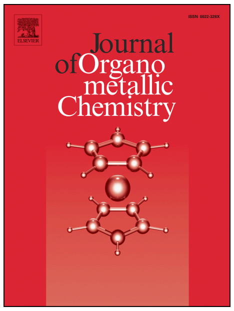


Ru(II) complexes bearing 2,6-bis(benzimidazole-2-yl)pyridine ligands: A new class of catalysts for efficient dehydrogenation of primary alcohols to carboxylic acids and H_2 in the alcohol/CsOH system

Zengjin Dai, Qi Luo, Xianggao Meng, Renjie Li, Jing Zhang, Tianyou Peng

PII: S0022-328X(16)30551-4

DOI: 10.1016/j.jorganchem.2016.11.038

Reference: JOM 19723

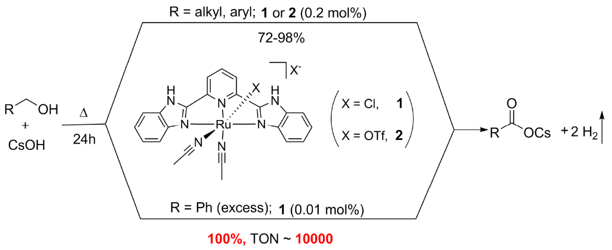
To appear in: *Journal of Organometallic Chemistry*

Received Date: 22 August 2016

Revised Date: 28 November 2016

Accepted Date: 29 November 2016

Please cite this article as: Z. Dai, Q. Luo, X. Meng, R. Li, J. Zhang, T. Peng, Ru(II) complexes bearing 2,6-bis(benzimidazole-2-yl)pyridine ligands: A new class of catalysts for efficient dehydrogenation of primary alcohols to carboxylic acids and H_2 in the alcohol/CsOH system, *Journal of Organometallic Chemistry* (2017), doi: 10.1016/j.jorganchem.2016.11.038.


R = alkyl, aryl; **1** or **2** (0.2 mol%)
72-98%
R OH
+
CsOH
Δ
24h
X⁻
X
N
H
Ru
X = Cl, 1
X = OTf, 2
O
R OCs
+2 H2
R = Ph (excess); **1** (0.01 mol%)
100%, TON ~ 10000

Ru(II) Complexes Bearing 2,6-Bis(benzimidazole-2-yl)pyridine Ligands: A New Class of Catalysts for Efficient Dehydrogenation of Primary Alcohols to Carboxylic Acids and H_2 in the Alcohol/CsOH System

Zengjin Dai,[a] Qi Luo,[a] Xianggao Meng,[b] Renjie Li,[a] Jing Zhang,[a*] and Tianyou Peng[a*]

[a] College of Chemistry and Molecular Science, Wuhan University, Wuhan 430072, P. R. China

[b] Key Laboratory of Pesticide and Chemical Biology, Ministry of Education; School of Chemistry, Central China Normal University, Wuhan430079, P. R. China

[*] Tel./Fax: +86 27 6875 6679. E-mail: jzhang03@whu.edu.cn (J. Zhang); typeng@whu.edu.cn (T. Peng)

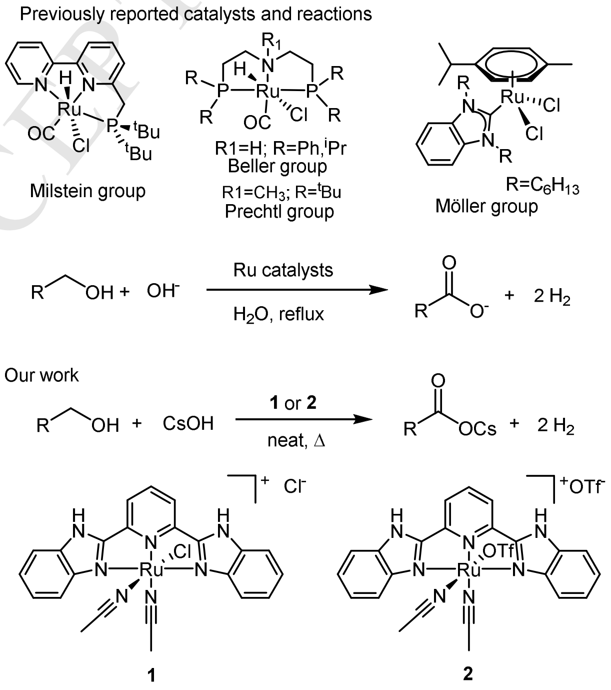
ABSTRACT: Mono-cationic Ru(II)-complexes [Ru(**L**)X(CH_3CN)$_2$]·X **1~4** (**1**, **L**=2,6-bis(benzimidazol-2-yl) pyridine (**L1**), X=Cl; **2**, **L**=**L1**, X=OTf; **3**, **L**=2-(N-benzyl-benzimidazole-2-yl)-6-(benzimidazole-2-yl)pyridine (**L2**), X=Cl**; 4, L =** 2,6-bis(N-benzyl-benzimidazole-2-yl)pyridine (**L3**), X=Cl) were prepared and fully characterized. The two acetonitrile ligands of each complex are coordinated to the metal center *cis* to each other. Complex **2** was also structurally characterized by X-ray crystallography. It was found that complexes **1**~**4** can catalyze the acceptorless dehydrogenation of primary alcohols to corresponding carboxylic acids and H_2 in the basic aqueous solution, and the reactivity follows the order **1** = **2** > **4** > **3**. Furthermore, complexes **1** or **2** can efficiently catalyze the conversion of various primary alcohols to carboxylic acid in good yields (72%~98%) and high selectivity in an alcohol/CsOH system (1/1, mol/mol). Using an excess amount of alcohol to CsOH results in the formation of the carboxylic acid in higher yield (up to 100%, based on CsOH) and higher turnover numbers (TON ~ 10000) accompanied by the H_2 evolution. Complexes **1** and **2** can act as a new class of phosphine- and N-heterocycle carbene free Ru(II) complexes for efficient conversion of primary alcohols to carboxylic acids and H_2 in a homogeneous system.

Keywords: N′NN′ pincer ligands; Ru(II) complex; acceptorless dehydrogenation; carboxylic acid; H_2 production

1. Introduction

In the past decade, Ru(II) complexes with “bulky” pincer ligands have been well demonstrated for catalytic acceptorless dehydrogenation of primary alcohols to esters [1], amides [2], aldehydes [3] and imines [4], which presents a “green” pathway for transforming alcohols to carbonyl derivatives. However, the pincer ligands in these Ru(II) pincer systems reported normally contains at least one phosphine or N-heterocycle carbene donor, which are essentially sensitive to O_2 or the moisture. It is worthy to develop new metal pincer systems in which the ligands contain only N or O donors and can be prepared through a simple and low energy-consuming procedure. In 2013, Szymczak’s group [5] reported a NNN-amide Ru(II) hydride complex which can efficiently dehydrogenate alcohols to ketones or esters and H_2, but this complex still contains two triphenylphosphine ligands. Although a Ru(II) complex with a quadridentate bis(olefin)diazidiene ligand was used to efficiently catalyzed the dehydrogenation of MeOH/H_2O to CO_2 and H_2 in a basic aqueous system, the conversion of other primary alcohols to the corresponding carboxylic acids was not reported [6]. Up to now, the examples of ruthenium(II) complex based on NNN-typed pincer ligand are scarce to the best of our knowledge.

Carboxylic acids and salts are important chemicals in both laboratory and industry. One of the promoting synthetic processes of carboxylic acids is direct oxidation of primary alcohols in one step [7]. However, most of the reported methods have been performed by using stoichiometric amounts of toxic oxidation reagents [8], highly pressurized dioxygens [9], or additional sacrificial substrates as the hydrogen acceptors [10]. So far only three Ru(II) systems have been developed for efficient dehydrogenation of primary alcohols to carboxylic acid and H_2 in a basic aqueous solution[11-14] (Scheme 1). It is noted that an excess amount of water is necessary in these systems in order to increase the selectivity of carboxylic acid. Milstein and co-workers[11] firstly presented a Ru(II)-PNN′ typed complex (Scheme 1), which acceptorlessly converts various primary alcohols to carboxylic acid salts in a basic aqueous solution. The yields are 61~91% when the ratio of substate/catalyst is 500/1 (mol/mol)). Similarly, Beller and co-workers[12a] reported a Ru(II)-PNP complex (Scheme 1), which can convert ethanol to acetic acid and H_2 in a NaOH-water solution with high turnover numbers (TON ~80000) when the reaction was performed for 96 h. However, the amount of by-products (a mixture of 1-butanol and ethyl acetate) increased to 30% yield when the ratio of water/ethanol was 1/9 (v/v), while the sole product of acetic acid was obtained in a 1/3 (v/v) ratio of water/ethanol solution. Herein, we report four Ru(II) complexes based on 2,6-bis(benzimidazole-2-yl)pyridine (N′NN′) ligands, which efficiently catalyze the acceptorless dehydrogenation of primary alcohols to carboxylic acids and H_2 in a homogeneous alcohol-CsOH system. The reactivity of our complexes can be compared to the reported Ru(II) complexes bearing the ligands with phosphine- or N-heterocycle carbene donors [11~14]. Although several Ru(II) complexes with 2,6-bis(benzimidazole-2-yl)pyridine or 2,6-bis(imidazole-2-yl-)pyridine ligands have been found uses in transfer hydrogenation of ketones[15], anion-sensor[16], aerobic oxidation of alcohols to imine [17], and C-H bond activation [18]. None of them has been applied in the acceptorless alcohol dehydrogenation to the best of our knowledge.



Scheme 1. Catalytic dehydrogenation of primary alcohols to carboxylic acid salts and H_2

2. Results and Discussion

2.1 Synthesis and Characterization of Ru(II) Complexes 1~4:

N′NN′ pincer ligand 2,6-bis(benzimidazole-2-yl)pyridine (**L1**) was prepared from pyridine-2,6-dicarboxylic acid and benzene-1,2-diamine according to the known method[19]. 2,6-bis(N-benzyl-benzimidazole-2-yl)pyridine (**L3**) was synthesized from **L1** with an excess of benzyl bromide [15b]. The new ligand 2-(N-benzylbenzimidazole-2-yl)-6-(benzimidazole-2-yl)pyridine (**L2**) was synthesized from **L1** with one equivalent of benzyl bromide in a modest yield (57%) by using a slightly modified procedure for the synthesis of **L3**. When **L1** and 0.5 equivalent of $[RuCl_2(p\text{-cymene})]_2$ were heated in acetonitrile for 12h, complex [RuCl(**L1**)$(MeCN)_2$]·Cl (**1**) was obtained in good yield (88%). The ^1H NMR spectrum of **1** shows two singlet peaks with the integration of three protons each at 2.06 and 3.17 ppm, which can be assigned to the CH_3 groups of two acetonitrile ligands. This observation indicates the two acetonitrile ligands are coordinated to the metal center in the axial and equatorial positions, respectively [20], which is further confirmed by the ^{13}C NMR and HSQC spectra (see supporting information). A neutral complex [$RuCl_2$(**L1**)(MeCN)] was previously reported by Dayan *et al* through a procedure similar to ours [15c].

Complex [Ru(OTf)(**L1**)$(MeCN)_2$]·(OTf) (**2**) was prepared by the extraction of two chlorides from **1** with two equivalents of AgOTf in methanol. The ^1H NMR spectrum of **2** exhibits a singlet peak at 14.95 ppm for the two magnetic equivalent N-H moieties of **L1**, presenting an upfield shift of 0.22 ppm relative to that of **1** (δ 15.17 ppm). The two magnetically nonequivalent acetonitrile ligands of **2** are also confirmed by its ^1H NMR spectrum which shows two singlet signals with equal integration of three protons at 2.09 and 3.20 ppm, respectively. For further characterization of **2**, single crystals suitable for X-ray diffraction study were obtained by slow diffusion of diethyl ether into a concentrated 2,2,2- trifluoroethanol solution of **2**. Although the crystal data are not very satisfied, the structure of **2** still clearly displays the Ru(II) center adopt a distorted octahedral coordination geometry with the coordination plane defined by three N atoms of **L1** and one N atom of acetonitrile, while another acetonitrile ligand and one water ligand occupy the axial positions (Fig. **1**). The water is probably from the solvents since the 2,2,2-trifluoroethanol was simply treated by the distillation from commercially available reagent. The bond distance of Ru(1)-N(7) (2.053(8) Å) is larger than that of Ru(1)-N(6) (1.994(9) Å), which is consistent with the larger *trans* effect of pyridyl N atom relative to that of water O atom. The bond distances of Ru(II)-N(pyridyl) and Ru(II)-N(benzimidazol-2-yl) match well with other reported Ru(II)-**L1** and Ru(II)-terpyridines complexes[15, 21]. The bond angle of N(6)-Ru(1)-N(7) (94.1(3) Å) confirms the two acetonitrile ligands are coordinated to the metal center *cis* to each other, which is consistent with the observations in its ^{1}H NMR and ^{13}C NMR spectra.

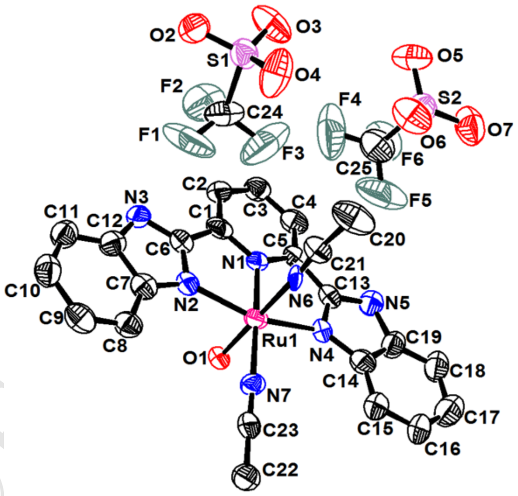
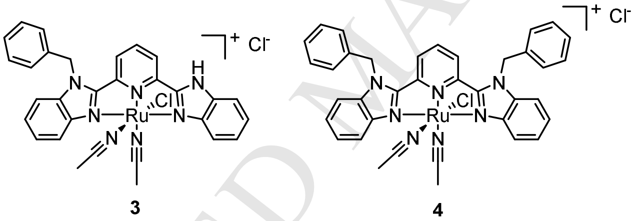


Figure 1. The structure of **2**·H_2O with thermal ellipsoids drawn at the 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths(Å): Ru1-N1, 1.982(8); Ru1-N2, 2.080(8); Ru1-N4, 2.076(8); Ru1-N6, 1.994(9); Ru1-N7, 2.053(8); Ru1-O1, 2.090(7); Selected bond angles(°): N1-Ru1-N6, 90.0(3); N1-Ru1-N7, 175.9(3); N6-Ru1-N7, 94.1(3); O1-Ru1-N6, 177.8(3).

In comparison with **1**, complexes [Ru(**L2**)Cl(CH_3CN)$_2$]·Cl **3** and [Ru(**L3**)Cl(CH_3CN)$_2$]·Cl **4** were synthesized from $[RuCl_2(p\text{-cymene})]_2$ with **L2** and **L3** by using the procedure similar to the one used for **1**, respectively (Scheme 2). The structures of **3** and **4** are similar to that of **1**. The ^{1}H NMR spectrum of **3** shows one singlet peak with integration of two protons at 6.35 ppm, which is assigned to the benzyllic $-CH_2-$ of **L2**. In addition, the two acetonitrile ligands of **3** with different chemical environments are confirmed by its ^{1}HNMR spectrum, which exhibits two singlet signals at 2.07 and 3.19 ppm with equal integration of three protons, respectively. Similarly, the two acetonitrile ligands of **4** attached to the metal center *cis* to each other is also approved by its ^{1}H NMR (two singlet signals with integration of three protons each at 2.09 and 3.22 ppm for the $-CH_3$ moiety, respectively) and its ^{13}C NMR (two singlet peaks at 3.48 and 4.50 ppm for the $-CH_3$ moiety, respectively) spectra. No signal is observed at 9~16 ppm in the ^{1}H NMR spectrum indicates the absence of N-H of **4**.



3

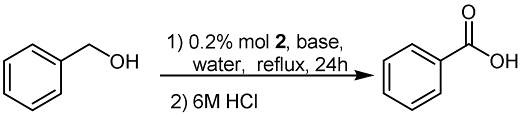
4

Scheme 2. The structures of complexes **3** and **4**.

2.2. Catalytic dehydrogenation of primary alcohols

In preliminary studies, benzyl alcohol was chosen as the substrate for the acceptorless dehydrogenation. A typical reaction was carried out under argon atmosphere by using **2** as the catalyst precursor (0.2 mol% to the alcohol) in the basic aqueous solution (bi-phase) with the procedure reported by Milstein *et al* [11]. When KOH was used as the base, benzoic acid was obtained in 19% yield (TON 95) after 24h (Table 1, entry 1). After optimizing the effect of various bases, we found that the highest yield of benzoic acid was obtained (37%, TON ~ 185) with the use of CsOH (Table 1, entry 5). Using weaker bases (LiOH or Na_2CO_3) afforded relatively lower yields (6% and 4%, respectively) (Table 1, entry 3 and 4). As expected, almost no benzoic acid was observed without the base under the same condition (Table 1, entry 6).

Table 1. Base screening for the catalytic reaction in alcohol-water system

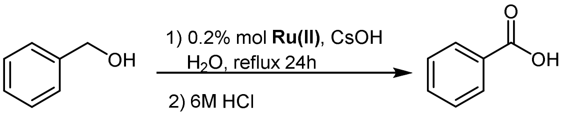


Entry	Base	Yield [a, b] (%)
1	KOH	17
1	NaOH	21
3	$LiOH\cdot H_2O$	6
4	Na_2CO_3	4
5	$CsOH\cdot H_2O$	37
6	none	< 2

[a] Reaction condition: benzyl alcohol (5mmol), base (5.5mmol), catalyst **2** (10μmol), H_2O (2mL) were refluxed in an oil bath under an argon atmosphere. [b] Isolated yield of benzoic acid=n (acid)/n (alcohol). Benzoic acid was obtained by acid treatment of the salts.

When a solution of benzyl alcohol and 1.5 equivalents of $CsOH\cdot H_2O$ with 0.2 mol% of **2** was refluxed for 24h, benzoic acid was obtained in 44% yield (Table 2, entry 2), suggesting the use of an excess amount of base just afforded slightly higher yield. As expected, prolonging the reaction time to 72h resulted in the formation of benzoic acid in the higher yield (82%) (Table 2, entry 3). Complex **1** shows almost the same catalytic activity with **2** under the same condition (Table 2 entry 1 and 2), probably because of the same intermediates formed in the catalytic cycle by extraction of chloride or triflate anions with hydroxide anions from **1** and **2**, respectively. However, when complex **3** or **4** was tested instead of **2**, benzoic acid was obtained in the relatively low yield (10% and 28%, respectively), indicating the two N-H groups of **L1** play an important role in the catalytic cycle.

Table 2. Catalyst screening for the catalytic reaction



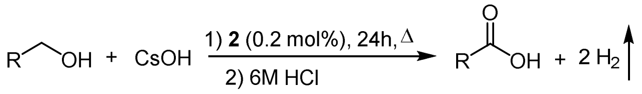
Entry	Catalyst	Yield [a] (%)
1	**1**	44
2	**2**	44
3	**2**	82 [b]
4	**3**	10
5	**4**	28
6	none	<1

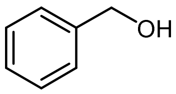
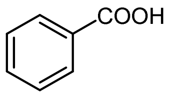
[a] Reaction condition: benzyl alcohol (5mmol), $CsOH \cdot H_2O$ (7.5mmol), catalyst (10μmol), H_2O (2mL) were refluxed in an oil bath under an argon atmosphere for 24h, isolated yield of benzoic acid=n (acid)/n (alcohol). [b] The reaction time is 72h.

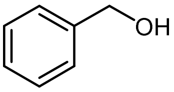
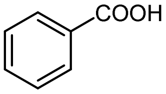
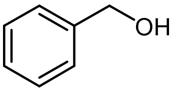
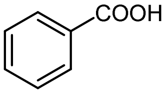
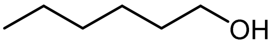
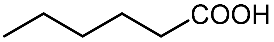
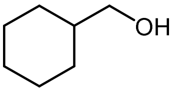
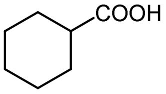
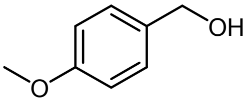
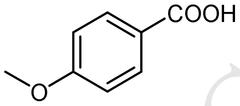
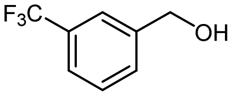
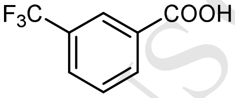
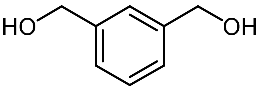
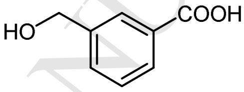
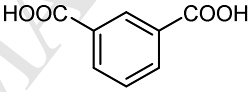
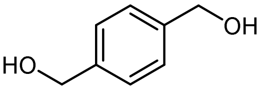
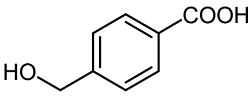
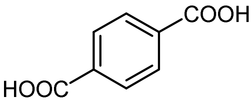
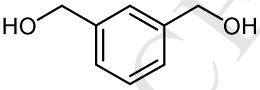
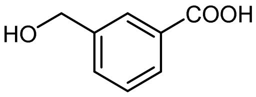
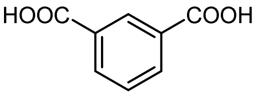
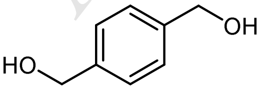
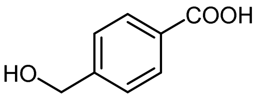
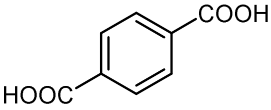
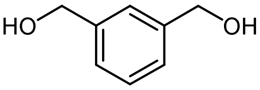
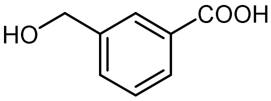
Since OH^- can be used as the oxygen source for the conversion of alcohol to carboxylic acid, and the existence of large amount of water reduces the concentration of the base, we think reducing the amount of water might benefit the alcohol coordinated to the Ru(II) center, followed by the β-H elimination of alkyloxide occurring to produce the aldehyde as the initial step of the catalytic cycle. So, further investigations were carried out in the homogeneous alcohol-CsOH system. To our delight, when benzyl alcohol and one equivalent of $CsOH \cdot H_2O$ with 0.2 mol% of **2** were heated at 150°C (oil bath) under an argon atmosphere for 7 minutes, the evolution of H_2 gas (confirmed by the GC, see supporting information) was observed from the initial homogeneous solution, accompanied by the formation of cesium benzoate as a white solid. The benzoic acid was achieved in 75% yield after 4h (Table 3, entry 1), presenting the reaction rate is much faster than that in water-alcohol bi-phase system (72h, 82%). However, only 80% yield of benzoic acid was obtained when the reaction time was 24h, probably because of the formation of benzoate salt solidifying the reaction solution. The unreacted benzyl alcohol was recovered in 17% yield, and the small amounts of benzaldehyde and benzyl benzoate (total lower than 2%) were detected by GC-MS and ^{1}H NMR spectrum (see supporting information). Under such condition, using an excess amount of CsOH afforded a lower yield (75%, 24h) (Table 3, entry 3).

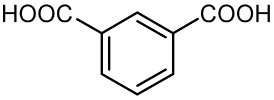
Under the optimized reaction conditions, other primary alcohols can also be dehydrogenated to the corresponding carboxylic acids in good yields by using complex **2** as the catalyst (Table 3). When 4-methoxybenzyl alcohol and one equivalent of $CsOH{\cdot}H_2O$ with 0.2 mol% of **2** were heated at 150°C for 24h, 4-methyloxy-benzoic acid was obtained in 84% yield. While 3-trifluoromethylbenzyl alcohol was used as a substrate, 3-trifluoromethyl benzoic acid was obtained in 57% yield (Table 3, entry 6 and 7), probably because of the electron-withdrawing group of the aromatic alcohol reducing the nucleophilicity of the alcohol to the Ru(II) center, which is important in the dehydrogenation. Various diols can be converted to a mixture of monocarboxylic acids and di-carboxylic acids in good yields (75~98%) under the similar condition (Table 3, entry 8-11). As expected, a longer reaction time resulted in the formation of di-carboxylic acid in the higher yield (Table 3, entry 12). Aliphatic alcohols can also be efficiently dehydrogenated to carboxylic acid in good yields. For example, the hexylic acid was obtained in 77% isolated yield when 1-hexanol was loaded (Table 3, entry 4). In all cases, the unreacted alcohols can be recovered within 3% lose.

Table 3. Dehydrogenation of alcohols to carboxylic acid in a 1:1 (mol/mol) ratio of alcohol/CsOH



Entry	Alcohol	Base (equiv.)	Products	Yield [a] (%)
1		1.0		75 [b]

2		1.0		80
3		1.5		75
4		1.0		77
5		1.0		72
6		1.0		84
7		1.0		57
8		1.0	 	52 [c] 23 [c]
9		1.0	 	80 [c] 8 [c]
10		2.0	 	39 [c] 50 [c]
11		2.0	 	30 [c] 56 [c]
12 [d]		2.0		10 [c]

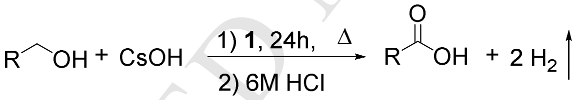
		88 [c],

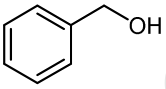
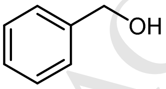
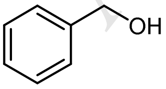
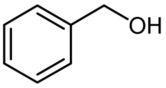
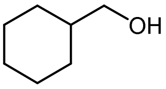
[a] Reaction condition: alcohol (entries 1-7, 5mmol; entries 8-12, 2.5mmol), CsOH·H_2O (entries 1-2, 4-7 and 10-12, 5mmol; entries 8-9, 2.5mmol; entry 3, 7.5mmol), catalyst (entries 1-7, 10μmol; entries 8-12, 5μmol) were heated under 150°C. [b] The reaction time is 4h. [c] The ratio of mono-carboxylic acid and di-carboxylic acid was determined by the ^1H NMR of the mixed acid isolated from the reaction mixture. Carboxylic acids were obtained by acid treatment of the salts. [d] The reaction time is 48h.

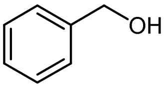
In many cases, the large amounts of carboxylic acid salts precipitate from the reaction solution, and the magnetic bar stop stirring, so the dehydrogenation rate decreases quickly. This problem might be overcome by adding proper solvents to the reaction system. However, the addition of normal solvents such as THF, 1, 4-dioxane, toluene *etc* did not afford the higher yield of carboxylic acid. We think using an excess of alcohol may promote the reaction. When a solution of benzyl alcohol and 0.5 equivalent of CsOH·H_2O with 0.1 mol% of **1** was heated at 150°C for 24h under an argon atmosphere, benzoic acid was obtained in 95% yield (based on the CsOH) (Table 4, entry 1), presenting the higher yield and higher TON (~475) than that in a 1/1 (mol/mol) ratio of benzyl alcohol/CsOH·H_2O system (80% yield). Upon increasing the ratio of benzyl alcohol /CsOH to 5/1 (mol/mol), the reaction completed after 2.5 h and the benzoic acid was obtained in 94% isolated yield (Table 4, entry 2), which is consistent with the H_2 production test (table 5). Moreover, with a lower catalyst loading, the carboxylic acids were also obtained in high yields (Table 4, entries 3~5). For example, when 0.01 mol% of **1** and CsOH·H_2O (25 mmol) in the excess of benzyl alcohol (125 mmol) were heated at 150°C for 24h, benzoic acid was obtained in quantitative yield with the TON ~ 10000 (Table 4 entry 4). As expected, using anhydrous NaOH as a base resulted in the formation of benzoic acid in only 33% yield (TON 3300) under the same condition (table4, entry 6). For reasons that remain to be determined CsOH gives much better results than NaOH, we think the concentration of alkyloxide anion play an important role in our reaction system. Since

CsOH is a stronger base than NaOH or KOH in the alcohol solution, the use of CsOH results in a higher concentration of alkyloxide anion according to the equilibrium: $ROH + MOH \rightleftharpoons RO^- + M^+ + H_2O$. In addition, CsOH may neutralize the carboxylic acid more efficiently than other metal hydroxides in the alcohol solvent, which is favor to the dehydrogenation of alcohol [11]. In the case of benzyl alcohol used, the solid benzoate salt can be easily isolated by filtration, and the remaining solution is subjected to the second catalytic cycle without obviously catalytic efficiency decrease (see supporting information). For example, the total yield of benzoic acid was 98% with TON ~ 19600 in the two round cycles. When cyclohexylmethanol was used as the substrate under the similar condition, cyclohexanecarboxylic acid was obtained in 83% yield with TON ~ 8300 after 24h (table 4, entry 5), which is higher than that in a 1/1 ratio of cyclohexylmethanol/CsOH system (72%, TON ~ 360).

Table 4. Catalytic dehydrogenation with excess alcohol as the solvent



Entry	Alcohol	n(alcohol/base)	Catalyst (mol%)	Reaction time(h)	Yield [a, b] (%)	TON [c]
1		2:1	0.2	24	95	475
2		5:1	0.2	2.5	94	470
3		5:1	0.02	24	100	5000
4		5:1	0.01	24	100	10000
5		5:1	0.01	24	83	8300

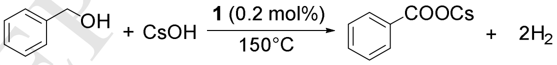
6[d]		5:1	0.01	24	33	3300

[a] Reaction condition: For entries 1-2. Alcohol (entry 1, 10mmol; entry 2, 25mmol), $CsOH\cdot H_2O$ (5mmol), catalysts (10μmol) were stirred and heated under argon; for entries 3-6. Alcohol (125mmol), $CsOH\cdot H_2O$ (25mmol), catalyst (entry 3, 5μmol; entries 4-6, 2.5μmol) were stirred and heated under argon. [b] Isolated yield=n (acid)/n (CsOH)); [c] TON=n (acid)/n (catalyst); [d]NaOH was used as the base.

2.3. The H_2 Production from catalytic dehydrogenation of benzyl alcohol

The formation of H_2 from the catalytic system was confirmed by GC analysis (see supporting information) and quantified by the gravity drainage method according to the reported literature [12]. The typical reaction was carried out under an argon atmosphere by using 0.2 mol% of **1** and $CsOH\cdot H_2O$ (5 mmol) in an excess of benzyl alcohol (25 mmol). The results are listed in table **5**. It is noted that the H_2 gas was observed in 74.2% (based on CsOH) after 1h and the catalytic reaction completed after 2.5h. The total amount of H_2 was double mol to that of CsOH, which is consistent with the isolated yield of benzoic acid (94%).

Table 5. The H_2 production during the catalytic reaction



Time (h)	Hydrogen Gas Volume (mL)	n (mmol)	TON (H_2)	TOF (h^{-1})
0.25	38	1.57	157	628
0.5	82	3.38	338	676
1.0	180	7.42	742	742
1.5	223	9.20	920	614
2.0	233	9.62	962	480

2.5	243	10.03	~1000	400
3.0	250	10.06	~1000	-

Reaction condition: Benzyl alcohol (25mmol), CsOH·H_2O (5mmol), and complex **1** (10μmol) were heated under argon. A blank experiment without catalyst was taken at the same time.

The standard atmospheric pressure P=101.325KPa; room temperature T=289.15K; the corresponding water saturated vapor pressure under the temperature P_0=1.8185KPa. The approximate amount of H_2 was calculated by Van der Waals equation: $(P-P_0)V=nRT$ (R=8.314 KPa·L·mol^{-1}·K^{-1}). TON=n(H_2)/n(catalyst); TOF=TON/t.

3. Conclusion

We have demonstrated new Ru(II)-N′NN′ pincer complexes with high efficiency in dehydrogenation of primary alcohols to corresponding carboxylic acids and H_2 in the alcohol-base system. The highest yield was obtained by using CsOH as the base. The higher catalytic reactivity was achieved in the homogeneous alcohol-CsOH system than that in the alcohol-water bi-phase system, while only very small amounts of aldehydes and esters (total lower than 2%) were observed as the by-products. Moreover, the much higher yields (up to 100%) and high turnover number (TON ~ 10000) were obtained by using an excess of alcohol with a lower catalyst loading. Complexes **1** and **2** present a new example of phosphine- and N-heterocycle carbene free Ru(II) complexes with high efficiency for converting primary alcohols to carboxylic acids and H_2. Our work may open a thread to design new transition metal complexes for acceptorless dehydrogenation of alcohol to corresponding carbonyl derivatives. The investigation of the detail catalytic mechanism is underway.

4. Experimental Section

4.1. General Information

All experiments with metal complexes were carried out under a purified argon atmosphere using the standard schlenk techniques. Ethanol, n-butanol, 1-hexanol, cyclohexyl-methanol and benzyl alcohol were purified according to standard procedures under argon atmosphere. Other reagents were used as received. Solvents were degassed with argon or nitrogen and kept in the spherical reservoir bottle with 4Å molecular sieve. The ^{1}H and ^{13}C spectra were recorded at 300MHz/75MHz Varian Gemini 300 spectrometer. The ^{1}H NMR chemical shifts were referenced to the residual hydrogen signals of the deuterated solvent or TMS, and the ^{13}C NMR chemical shifts were referenced to the ^{13}C signals of the deuterated solvent. Compounds of **L1 [**19], $[RuCl_2(p\text{-cymene})]_2$ [22], **L3 [**15b] were synthesized according to published procedures.

4.2. Synthesis and characterization of Ru(II) complexes (1~4)

4.2.1. $[Ru(L1)Cl(CH_3CN)_2]\cdot Cl$ (**1**) Ligand **L1** (0.622 g, 2mmol) and $[RuCl_2\ (p\text{-cymene})]_2$ (0.616 g, 1mmol) were dissolved in acetonitrile (50 mL) and the solution was refluxed for 12h under an argon atmosphere. After cooling to room temperature, the red-brown precipitate was filtered, washed with diethyl ether (3×5 mL) and then dried under vacuum for 12h. Complex **1** was obtained as a red-brown power (1.0 g, 88%). ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 2.06 (s, 3H); 3.17 (s, 3H); 7.49-7.58 (m, 4H); 7.80 (d, J=8.0 Hz, 2H); 8.01 (d, J=7.3 Hz, 2H); 8.22 (t, J=8.0 Hz, 1H); 8.57 (d, J=8.0 Hz, 2H); 15.17 (s, 2H, -NH). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 3.86; 4.71; 114.07; 118.64; 121.62; 122.44; 125.04; 126.11; 129.95; 134.57; 136.09; 143.29; 152.61; 153.45. Elemental Anal. Calcd. for $C_{23}H_{19}N_7Cl_2Ru$(%): C, 48.85; H, 3.39; N, 17.34. Found: C, 48.90, H, 3.60, 17.12.

4.2.2. $[Ru(L1)(CH_3CN)_2(OTf)]\cdot OTf$ (**2**) Complex **1** (0.226 g, 0.400 mmol) and silver trifluoromethanesulfonate (0.206 g, 0.800 mmol) were dissolved in methanol (20 mL) and the mixture solution was stirred at room temperature for 4 hours in the dark under an argon atmosphere. After the white precipitate of AgCl were filtered off through a celite pad, the red solution was evaporated to dryness under vacuum. The yellow residue was then dissolved in ethanol (6 mL) and diethyl ether (30 mL) was added slowly to precipitate the brown micro-crystals, which was filtered, washed with diethyl ether (3 ×5 mL), and then dried under vacuum for 12h to yield **2** (0.275 g, 82%). ^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm): 0.5 (t, J=7.0Hz, 3H), 2.09 (s, 3H, CH_3-CN), 2.86 (p, 2H), 3.20 (s, 3H), 6.04 (t, J=4.8 Hz, 1H), 7.60-7.65 (m, J=7.7 Hz, 4H,), 7.89 (d, J=6.7 Hz, 2H), 8.06 (dd, J=6.0, 2.5 Hz, 2H), 8.44 (dd, J=22.7, 6.9 Hz, 3H), 14.95 (s, 2H, -NH). ^{13}C NMR (75 MHz, DMSO-d$_6$) δ (ppm): 4.10 (s), 4.78 (s), 17.21 (s), 19.23 (s), 59.73 (s), 62.93 (s), 114.58 (s), 118.05 (d), 118.76 (d), 122.24 (s), 123.48 (s), 126.28 (d), 131.77 (s), 134.68 (s), 138.56 (s), 143.15 (s), 157.07 (s), 153.58 (s). Elemental Anal. Calcd for $C_{27}H_{25}O_7N_7F_6S_2Ru$ (Contain one molecule of ethanol) (%): C, 38.66; H, 3.00; N, 11.69 Found: C, 38.26, H, 2.89, 11.42. A brown single crystal of **2**·H_2O suitable for X-ray diffraction analysis was obtained by slow diffusion of diethyl ether to a concentrated 2,2,2-trifluoroethanol of **2** at room temperature for several weeks.

4.2.3. 2-((N-benzylbenzimidazole-2-yl)-6-benzimidazole-2-yl)pyridine (**L2**). Under an argon atmosphere, a solution of **L1** (1.00g ,3.2mmol) and ^{t}BuOK (0.36g, 3.2mmol) in acetone (60mL) was stirred at room temperature for 1h, then the benzyl bromide (0.55g, 0.32mmol) was added dropwisely and the mixture was refluxed for another 12h. After cooling to room temperature, the solvent was evaporated, and the residue was extracted with a mixed solvent of CH_2Cl_2 / CH_3OH (10:1, V: V, 3×50 mL). The combined organic solution was evaporated under reduced pressure and the crude product of **L2** was purified by the column chromatography using silica gel (elute: CH_2Cl_2/ethyl acetate, 3/1 (V/V)). Yield: 0.75g (58%). ^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm): 6.35 (s, 2H), 6.97 (d, J=7.3 Hz), 7.27 (ddd, J=45.0, 25.6, 6.9 Hz, 7H), 7.62 (d, J=7.9 Hz, 1H), 7.96-7.68 (m, 3H), 8.16 (d, J=7.8 Hz, 1H), 8.29 (d, J=7.7 Hz, 1H), 8.40 (d, J=7.8 Hz, 1H), 12.54 (s, 1H). ^{13}C NMR (75 MHz, CDCl3) δ (ppm): 49.16 (s), 110.53 (s), 111.55 (s), 120.31 (s), 120.67 (s), 121.86 (s), 122.90 (s), 123.55 (s), 124.23 (d), 125.35 (s), 126.11 (s), 127.99 (s), 129.58 (s), 133.78 (s), 136.83 (s), 137.74 (s), 138.59 (s), 143.01 (s), 144.40 (s), 147.66 (s), 149.29 (s). Elemental Anal. Calcd for $C_{26}H_{19}N_5$ (%): C, 77.76; H, 4.47; N, 16.63. Found: C, 77.79; H, 4.77; N 16.44.

4.2.4. Ru(L2)(CH_3CN)$_2$Cl]·Cl (**3**). Ligand **L2** (0.15g, 0.373mmol) and [$RuCl_2$(p-cymene)]$_2$ (0.115g, 0.187 mmol) were dissolved in acetonitrile (15mL) and the solution refluxed for 12h under an argon atmosphere. After cooling to room temperature, the mixture was filtered, the crude products was further purified by the column chromatography using silica gel (elute: ethanol) and dried under vacuum to afford complex **3** as a red-brown solid (0.085g, 35%). ^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm): 2.07 (s, 3H), 3.19 (s, 3H), 6.35 (s, 2H), 7.23 (dd, J=67.2, 6.5Hz, 4H), 7.85-7.44 (m, 5H), 8.03 (d, J=13.7 Hz, 3H), 8.15 (t, 1H), 8.29 (d, J=8.2 Hz, 1H), 8.48 (d, 1H), 15.03 (br). ^{13}C NMR (75 MHz, DMSO-d6) δ (ppm): 48.11, 112.54, 113.90, 118.25, 121.78, 123.17, 124.85, 125.52, 126.15, 126.44, 128.31, 129.49, 130.00, 134.54, 135.53, 136.21, 136.36, 142.20, 142.88, 151.55, 152.27, 152.65, 153.70; Elemental Anal. Calcd for $C_{30}H_{25}N_7Cl_2Ru$ (%): C, 54.97; H, 3.84; N, 14.96. Found: C, 55.22; H, 4.05; N, 14.68.

4.2.5. Ru(L3)(CH_3CN)$_2$Cl]·Cl (**4**) Ligand **L3** (0.15g, 0.305mmol) and [$RuCl_2$(p-cymene)]$_2$ (0.094g, 0.153 mmol) were dissolved in a mixed solvent of acetonitrile (5mL) and ethanol (5mL) and then refluxed for 12h under an argon atmosphere. After cooling to room temperature, the solution was taken to dryness under vacuum, the residue was passed through the column chromatography using silica gel (elute: methanol) to afford pure **4** as a red brown powder (0.077g, 34%). ^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm): 2.09 (s, 3H), 3.22 (s, 3H), 6.34 (s, 4H), 7.49-6.99 (m, 11H), 7.65 (m, 4H), 7.86 (t, J=8.2 Hz, 1H), 7.95 (d, 2H), 8.10 (d, 2H), 8.25 (d, 2H). ^{13}C NMR (75 MHz, DMSO-d$_6$) δ (ppm): 3.48, 4.50, 48.12, 112.65, 118.77, 121.62, 122.75, 125.68, 126.12, 126.47, 128.26, 129.48, 130.57, 136.22, 136.45, 141.93, 151.40, 153.15. Elemental Anal. Calcd for $C_{37}H_{31}N_7Cl_2Ru$: C, 59.60; H, 4.19; N, 13.15. Found: C, 59.83; H, 4.30; N, 12.97.

4.3. General procedure for catalytic reactions

4.3.1. Method A [11]: Benzyl alcohol (0.54g, 5mmol), **2** (8.3mg, 0.01mmol), base (5.5mmol) and 2mL degassed water were mixed in a 25mL schlenk tube and the reaction mixture was refluxed for 24h in an open system under argon. After cooling to room temperature, the degassed water (5mL) was added and the mixture was extracted with diethyl ether (3 ×10 mL). The aqueous phase was acidified with 6M HCl and extracted with ethyl acetate (5 × 20mL). The combined organic phase were washed with brine (25mL), dried over anhydrous Na_2SO_4, and evaporated to dryness under reduced pressure, the pure benzoic acid was obtained and further characterized by ^{1}HNMR which is consist with the standard sample.

4.3.2. Method B: To a schlenk tube (25mL) benzyl alcohol (0.54g, 5mmol), complex **1** (or **2**, **3**, **4**) (0.01mmol), $CsOH\cdot H_2O$ (1.26g, 7.5mmol) and 2mL deionized water were added and the reaction mixture was refluxed for 24h in an open system under argon. After cooling to room temperature, the degassed water (5mL) was added and the mixture was extracted with diethyl ether (3 ×10mL). The aqueous phase was acidified with 6M HCl and extracted with ethyl acetate (5 ×20mL). The combined organic phase was washed with brine (25mL), dried over anhydrous Na_2SO_4, and evaporated under vacuum, the pure benzoic acid was obtained and weighed for calculating the yield, which was further characterized by its ^{1}HNMR which is consist with the standard sample.

4.3.3. Method C: Complex **2** (8.3 mg, 10μmol), $CsOH\cdot H_2O$ (0.84 g, 5 mmol), alcohol (5 mmol) was added to a 25 mL schlenk tube and the solution was heated at 150°C (oil bath) for 24h in an open system under argon. After cooling to room temperature, the degassed water (5mL) was added and the mixture was extracted with diethyl ether (3 ×10mL). A sample of ether phase was subjected to the GC-MS analysis and the residual solution was evaporated, then subjected to the NMR analysis. The aqueous phase was acidified with 6M HCl and extracted with ethyl acetate (5 ×20mL). The combined organic phase was washed with brine (25mL), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure, the pure carboxylic acid was collected and weighed for calculating the yield, which was further characterized by its ^{1}H NMR which is consist with the standard sample.

4.3.4. Method D: For substrates of benzyl alcohol and cyclohexylmethanol: To a 100 mL schlenk tube complex **1** (1.4mg, 2.5μmol), $CsOH\cdot H_2O$ (4.2g, 25mmol), and alcohol (125mmol) were added and then the solution was heated at 150°C (oil bath) for 24h in an open system under argon. After cooling to room temperature, the degassed water (20mL) was added and the mixture was extracted with diethyl ether (3 ×20mL). The ether phase was evaporated under vacuum and the residue was subjected to the GC-MS and the NMR analysis. The aqueous phase was acidified with 6M HCl and extracted with ethyl acetate (5 ×30mL). The combined organic solution was washed with brine (50mL), dried over anhydrous Na_2SO_4, and evaporated under vacuum, the pure acid was obtained and weighed for calculating the yield, which was further characterized by its ^{1}H NMR which is consist with the standard sample.

4.4. Procedure for H_2 gas production

Under an argon atmosphere, benzyl alcohol (2.70g, 25mmol), $CsOH\cdot H_2O$ (0.84g, 5mmol), and complex **1** (5.7mg, 0.01mmol) were added to a 25 mL schlenk tube which is connected with a gas collection instrument through gravity drainage method. The reaction mixture was heated at 150°C (oil bath). Over a period of time, the volume of the gas was recorded. A blank experiment without catalyst was taken at the same condition.

4.5. X-ray crystallography

A Bruker SMART APEX II diffractometer with graphite-monochromated Mo-Kα (λ= 0.71073 Å) was employed to collect the intensity data for the single crystal of **2**. The data was collected at about 100K using ω-scan techniques. The structure was solved by direct methods using SHELXL-97 [23]. Multi-scan empirical absorption corrections were applied to the data set using the program SADABS [24]. The structure was refined with SHELXL-97[23]. Hydrogen atoms bound to carbon were placed at calculated positions and refined using a riding mode. All non-hydrogen atoms were refined by full-matrix least squares on F^2 using the SHELXTL grogram package [25]. Cell refinement, data collection, and reduction were done by Bruker SAINT[26]. The crystallographic data is available in the SI as CIF file.

Acknowledgements

This work was supported by the Natural Science Foundation of China (21171134, 21573166), the Natural Science Fund of Hubei Province (2011CDB441), and the Funds for Creative Research Groups of Hubei Province (2014CFA007), China. We also thank Prof. Xianggao Meng for the support of X-ray diffraction analysis of **2** (CCDC 1449878) and Prof. Xiaojun Wu for NMR supporting and analysis.

Notes

The authors declare no competing financial interests.

References

[1] a) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, J. Am. Chem. Soc. *127*(2005) 10840-10841; b) C. Gunanathan, L.J.W. Shimon, D. Milstein, J. Am. Chem. Soc. 131(2009) 3146-3147; c) D. Spasyuk, D.G. Gusev, Organometallics 31 (2012) 5239-5242; d) M. Gargir, Y. Ben-David, G. Leitus, Y. Diskin-Posner, L.J.W. Shimon, D. Milstein, Organometallics 31(2012) 6207-6214; e) D. Spasyuk, S. Smith, D.G. Gusev, Angew. Chem. Int. Ed. 51 (2012) 2772-2775; f) M. Nielsen, H. Junge, A. Kammer, M. Beller, Angew. Chem. Int. Ed. 51(2012) 5711-5713; g) S. Chakraborty, P.O. Lagaditis, M. Förster, E.A. Bielinski, N. Hazari, M.C. Holthausen, W.D. Jones, S. Schneider, ACS Catal. 4 (2014) 3994-4003;

[2] a) C. Gunanathan, Y. Ben-David, D. Milstein, Science 317 (2007) 790-792; b) L.U. Nordstrøm, H. Vogt, R. Madsen, J. Am. Chem. Soc. 130 (2008) 17672-17673; c) N. J. Oldenhuis, V. M. Dong, Z. B. Guan, Tetrahedron 70 (2014) 4213-4218; d) D.G. Gusev, ACS Catal. 6(2016) 6967-6981.

[3] a) K.–I. Fujita, T. Yoshida, Y. Imori, R. Yamaguchi, Org. lett. 13 (2011) 2278-2281; b) R. Kawahata, K.–I. Fujita, R. Yamaguchi, J. Am. Chem. Soc. 134 (2012) 3643-3646.

[4] a) B. Gnanaprakasam, J. Zhang, D. Milstein, Angew. Chem., Int. Ed. 49 (2010) 1468-1471; b) M.A. Esteruelas, N. Honczek, M. Oliván, E. Oñate, M. Valencia, Organometallics 30 (2011) 2468-2471; c) A. Maggi, R. Madsen, Organometallics 31 (2012) 451-455; d) L.P. He, T. Chen, D. Gong, Z.P. Lai, K.–W. Huang, Organometallics 31 (2012) 5208-5211; e) E. Balaraman, D. Srimani, Y. Diskin-Posner, D. Milstein, Catal. Lett. 145 (2015) 139-144.

[5] K.–N. T. Tseng, J.W. Kampf, N.K. Szymczak, Organometallics 32 (2013) 2046-2049.

[6] R.E. Rodriguez-Lugo, M. Trincado, M. Vogt, F. Tewes, G. Santiso-Quinones, H. Grützmacher, Nat. Chem. 5 (2013) 342-346.

[7] a) M. Trincado, D. Banerjee, H. Grützmacher, Energy Environ. Sci. 7 (2014) 2464-2503; b) G. Tojo, Oxidation of Primary Alcohols to Carboxylic Acids: A Guide to Current Common Practice (Basic Reactions in Organic Synthesis), Springer, 2010.

[8] a) K. Bowden, I. Heilbron, E.R.H. Jones, B.C.L. Weedon, J. Chem. Soc. 1946, 39-45; b) A. Bowers, T.G. Halsall, E.R.H. Jones, A.J. Lemin, J. Chem. Soc. 1953, 2548-2560; c) J.G. Miller, A.C. Oehlschlager, J.W. Wong, J. Org. Chem. 48 (1983) 4404-4407.

[9] L. H. Zhou, M.Z. Chen, Y.Q. Wang, Y.L. Su, X.M. Yang, C. Chen, J. Xu, Applied Catalysis A: General 475 (2014) 347-354.

[10] a) T. Zweifel, J.–V. Naubron, H. Grützmacher, Angew. Chem. Int. Ed. 48 (2009) 559-563; b) M. Trincado, H. Grützmacher, F. Vizza, C. Bianchini, Chem. -Eur. J. 16 (2010) 2751-2757.

[11] E. Balaraman, E. Khaskin, G. Leitus, D. Milstein, Nat. Chem. 5 (2013) 122-125.

[12] a) P. Sponhol, D. Mellmann, C. Cordes, P.G. Alsabeh, B. Li, Y. Li, M. Nielsen, H. Junge, P. Dixneuf, M. Beller, ChemSusChem 7 (2014) 2419-2422; b) Y. Li, M. Nielsen, B. Li, P.H. Dixneuf, M. Beller, Green Chem 17 (2015) 193-198.

[13] J.–H. Choi, L.E. Heim, M. Ahrens, M.H. G. Prechtl, Dalton Trans. 43 (2014) 17248-17254.

[14] J. Malineni, H. Keul, M. Möller, Dalton Trans. 44 (2015) 17409.

[15] a) W.J. Ye, M. Zhao, W.M. Du, Q.B. Jiang, K.K. Wu, P. Wu, Z.K. Yu, Chem. –Eur. J. 17 (2011) 4737-4741; b) S. Günnaz, N. Özdemir, S. Dayan, O. Dayan, B. Çetinkaya, *Organometallics* 30 (2011) 4165-4173; c) O. Dayan, S. Dayan, İ. Kani, B. Çetinkaya, Appl. Organometal. Chem. 26 (2012) 663–670.

[16] D. Maity, S. Das, S. Mardanya, and S. Baitalik Inorg. Chem. 52 (2013) 6820.

[17] E. Sindhuja, R. Ramesh Tetra. Lett. 55 (2015) 5504.

[18]B. G. Hashiguchi, K.J.H. Young, M. Yousufuddin, W.A. Goddard III, and R.A. Periana J. Am. Chem. Soc. 132 (2010) 12542.

[19] X.J. Xu, Z.X. Xi, W.Z. Chen and D.Q. Wang, J. Coord. Chem. 60 (2007) 2287-2308.

[20] H.–F. Suen, S.W. Wilson, M. Pomerantz, J.L. Walsh, Inorg. Chem. 28 (1989) 786-791.

[21] a) M.-A. Haga, M.M. Ali, S. Koseki, K. Fujimoto, A. Yoshimura, K. Nozaki, T. Ohno, K. Nakajima, D.J. Stufkens, Inorg. Chem. 35 (1996) 3335; b) B. Mondal, V.G. Puranik, G.K. Lahiri, Inorg. Chem. 41 (2002) 5813; c) N. Chanda, D. Paul, S. Kar, S.M. Mobin, A. Datta, V.G. Puranik, K.K. Rao, G.K. Lahiri, Inorg. Chem. 44 (2005) 3499; d) S. Sarkar, B. Sarkar, N. Chanda, S. Kar, S.M. Mobin, J. Fiedler, W. Kaim, G.K. Lahiri, Inorg. Chem. 44 (2005) 6092; e) N. Chanda, S. M. Mobin, V. G. Puranik, A. Datta, M. Niemeyer, G. K. Lahiri, Inorg. Chem. 43 (2004) 1056; f) A. Singh, G. Gas, B. Mondal, Polyhedron 27 (2008) 2563; g) S. Gunnaz, N. Özdemir, S. Dayan, O. Dayan, B. Çetinkaya, Organometallics 30 (2011) 4165-4173; h) D. Maity, S. Das, S. Mardanya, S. Baitalik, Inorg. Chem. 52 (2013) 6820-6838.

[22] M.A. Bennett, T.N. Huang, T.W. Matheson, A.K. Smith, Inorg. Synth. 21 (1982) 74.

[23]G.M. Sheldrick, SHELXL-97, Program for the solution of Crystal Structures, University of Gottingen, Germany, 1990.

[24] SADABS, Bruker Nonius area detector scaling and absorption correction, version 2.05, Bruker AXS Inc., Madison, WI, 1996.

[25] G.M. Sheldrick, SHELXL 5.10 for windows NT, Structure Determination Software Programs, Bruker AXS Inc., Madison, WI, 1997.

[26] SAINT, version 6.02, Bruker AXS Inc., Madison, WI, 1999.

Synthesis of ruthenium(II) complexes bearing rigid N′NN′-typed pincer ligands;

Catalytic dehydrogenation of primary alcohols to carboxylic acids and H_2;

Higher yields and higher selectivity obtained in homogeneous alcohol-CsOH system

Quantitative yield of benzoic acid and TON~10000 achieved in 24h.