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FULL PAPER

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Facile oxidation of alcohols to carboxylic acids in basic water medium by employing ruthenium picolinate cluster as an efficient catalyst

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Selective transformation of alcohols into carboxylic acids is a crucial process in industry for the synthesis of bulk chemicals. Current methods for the production of acids involve oxygen under pressure or toxic reagents like ruthenium chlorite or iodate or chromium oxides. Herein, we report the preparation of $[Ru_3(CO)_8(C_5H_4NCO_2)_2]$ cluster which is an efficient catalyst precursor for the conversion of primary alcohols into carboxylic acids under aerobic conditions. The catalytic process involves the use of NaOH in a water–isopropanol medium which gives a 90% yield of carboxylic acid (90% yield for benzoic acid in standard reaction). This clean process appears to be safe for the synthesis of various benzoic acids for both laboratory and also industrial purposes.

KEYWORDS
carboxylic acid, hydrobenzoin, monoclinic, picolinate ligands, $Ru_3(CO)_{12}$ cluster

1 | INTRODUCTION

Benzoic acid and its derivatives are important precursors for the synthesis of useful organic compounds.[1–4] Several hundred thousand tons of benzoic acid for industrial applications is produced every year.[5,6] Benzoic acid is a main component in food preservatives[7] mostly because of its antifungal[8,9] and antimicrobial activities.[9] Its derivatives are also useful for the production of plasticizers,[10] alkyd resins[11,12] and polymers.[13,14]

In the past few decades, the use of transition metal complexes has contributed tremendously to catalytic organic synthesis.[15–21] Oxidations of alcohols to carboxylic acids require various oxidants in large quantity, like $KMnO_4$, iodosobenzene, *t*-BuOOH and chromium oxide, and thus produce copious waste.[22] Whereas, the catalytic synthesis of carboxylic acid derivatives from alcohols was initially performed with ruthenium hydride complexes, polyoxometallates or PNN pincer complexes.[23–26]

Rhodium-catalysed oxidation of alcohol to carboxylate at high pH and using ketone as a hydrogen acceptor under mild conditions was reported by Grützmacher and co-workers.[27] A heterogeneous copper system[28] with NaOH at 320°C under high pressure has also been used for catalytic oxidation of alcohols to carboxylates.[29] For the oxidation of alcohols to carboxylic acids, a new clean and atom-economic approach has been introduced by Milstein and co-workers using water as the oxygen donor in the presence of a base and using a ruthenium hydride PNN pincer catalyst.[30] The reaction takes place with dehydrogenation of alcohol to give coordinated

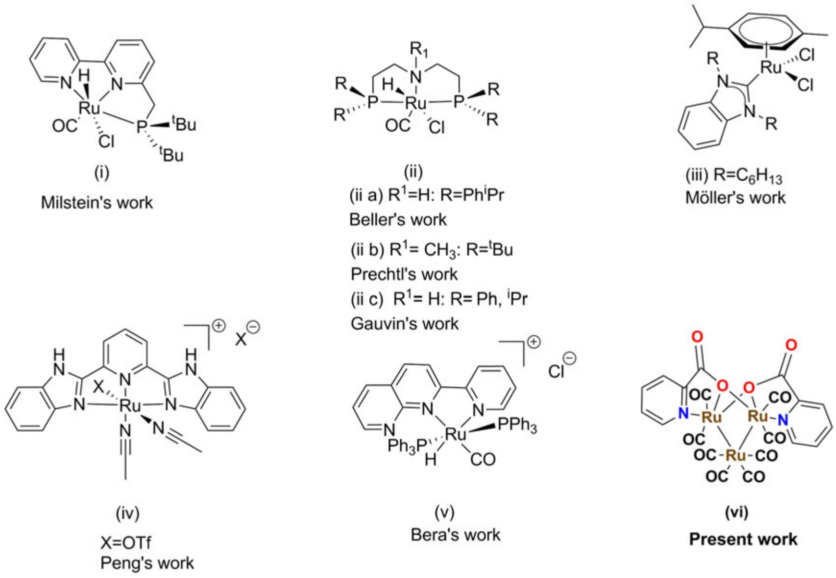
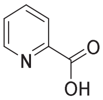
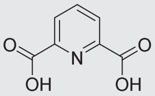
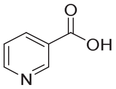
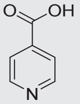


FIGURE 1 Ruthenium-based active catalysts for carboxylic acid synthesis from alcohols.

aldehyde to which water addition allows the formation of carboxylic acid.[30] Prechtl and co-workers also reported carboxylic acid formation from alcohols using ruthenium hydride PNP pincer catalyst (Figure 1(ii,b))[31] and Beller and co-workers converted renewable glycerol into 2-oxopropanoic acid using ruthenium hydride PNP pincer complex (Figure 1(ii,a)).[32] By contrast, Möller and co-workers used a simple ruthenium (II)–N-heterocyclic carbene complex to perform this transformation (Figure 1(iii)).[33] Peng and co-workers used a ruthenium complex containing a new 2,6-bis(benzimidazole-2-yl)pyridine pincer ligand for this catalytic transformation (Figure 1(iv)),[34] whereas Gauvin and co-workers[35] have shown that recyclable PNP–ruthenium hydride catalysts, prepared *in situ* by addition of PNP ligand to [Ru(H)(X)(CO)(PPh_3)$_3$] (X = H, Cl), were efficient for the oxidation of primary alcohols into carboxylates (Figure 1(ii,c)).[35] Recently Bera and co-workers reported that this oxidation reaction could be efficiently performed using a non-pincer ruthenium hydride complex (Figure 1(v)).[36]

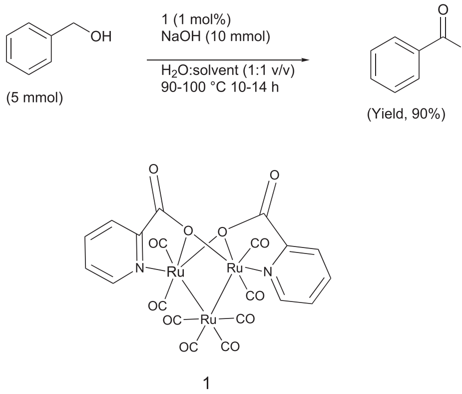
Most of the above mentioned efficient ruthenium catalysts for the transformation of alcohol to carboxylate in basic water involve ruthenium hydride or pincer ruthenium catalysts. In this report, we describe the preparation of a new ruthenium carbonyl cluster, namely [$Ru_3(CO)_8(C_5H_4NCO_2)_2$] (**1**), containing two simple

TABLE 1 Screening of catalyst for transformation of benzyl alcohol to benzoic acid in basic water and dioxane as solvent[a]

Entry	Component 1	Component 2	Adduct/cluster	Catalytic oxidation reaction[b]
1	$Ru_3(CO)_{12}$		**1**	R
2	$Ru_3(CO)_{12}$		**2**	R
3	$Ru_3(CO)_{12}$		**3**	NR
4	$Ru_3(CO)_{12}$		**4**	NR
5	$Ru_3(CO)_{12}$	—		NR

[a] Reaction conditions: benzyl alcohol (5 mmol), base (10 mmol), catalyst (1 mol%), H_2O (500 μl), solvent (500 μl) were stirred at bath temperature of 98°C in an oil bath in open atmosphere.

[b] R, reaction successful; NR, no reaction.



SCHEME 1 ■

chelating pyridine-carboxylate ligands (Figure 1(vi)), as an efficient catalyst, without pincer ligand, for the transformation of a variety of alcohols into carboxylic acids in basic water–isopropanol medium with good yields.

2 | RESULTS AND DISCUSSION

2.1 | Catalyst Screening

The oxidation of benzyl alcohol into carboxylic acid was carried out using a catalyst arising *in situ* from $Ru_3(CO)_{12}$ and a pyridine derivative containing a carboxylate group picolinic acid (**1a**), pyridine-2,6-dicarboxylic acid (**1b**), nicotinic acid (**1c**) and isonicotinic acid (**1d**) to afford the adducts **1–4**, respectively (Table 1). It was found that adduct/cluster **1** and adduct **2** were active in the catalytic transformation of alcohols to carboxylic acids using NaOH in an open atmosphere for 14 h at bath temperature of 98°C in water–solvent (Scheme 1) likely due to their appropriate five-membered chelation to $Ru_3(CO)_{12}$ which is not possible with nicotinic and isonicotinic acid ligands. The chelation environment is confirmed by the structure of cluster **1**. It was authenticated by single-crystal X-ray studies.

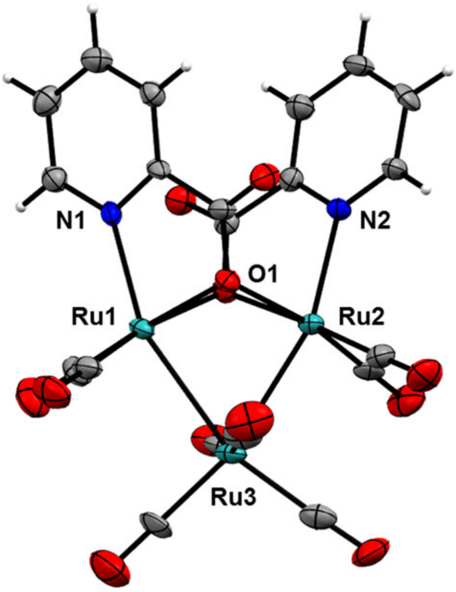


FIGURE 2 Perspective view of cluster **1**.

2.2 | Structural Description of Catalyst 1

Cluster **1** was obtained by reaction of $Ru_3(CO)_{12}$ with simple chelation of picolinic acid in toluene at 110°C for an hour. The molecular structure of **1** revealed the binding modes of picolinic acid ligand to $Ru_3(CO)_{12}$ and the crystal structure is shown in Figure 2. The detailed structural parameters of complex **1** are presented in Table 2.

TABLE 2 Crystal data and structure refinement for complex **1**

Identification code	Complex 1
Empirical formula	$C_{10}H_4NO_6Ru_{1.5}$
Formula weight	385.75
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	Pn
a (Å)	9.45480(10)
b (Å)	11.71470(10)
c (Å)	11.03310(10)
α (°)	90
β (°)	98.2050(10)
γ (°)	90
Volume (Å^3)	1209.52(2)
Z	4
ρ_{calc} (g cm^{-3})	2.118
μ (mm^{-1})	15.593
$F(000)$	740
Crystal size (mm^3)	0.34 × 0.33 × 0.29
Radiation	Cu Kα (λ = 1.54184 Å)
2θ range for data collection (°)	7.546 to 142.5
Index ranges	$-8 \le h \le 11$, $-14 \le k \le 14$, $-13 \le l \le 13$
Reflections collected	6597
Independent reflections	3023 [R_{int} = 0.0467, R_{sigma} = 0.0271]
Data/restraints/parameters	3023/2/334
Goodness-of-fit on F^2	1.091
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0487, wR_2 = 0.1282
Final R indexes [all data]	R_1 = 0.0494, wR_2 = 0.1343
Largest diff. peak/hole (e Å^{-3})	1.52/−1.43
CCDC no.	1576762

The structure of **1** is symmetric and it crystallized in *P*n space group with monoclinic crystal system. In this structure, the asymmetric unit consists of one picolinate ligand attached to one ruthenium atom by the nitrogen atom and one oxygen atom. The oxygen of the picolinate ligand is bridging the two ruthenium atoms, each adopting a distorted octahedral $RuC_2N_1O_2$ coordination sphere (Figure 2). The unique O–Ru–O *cis* bite angle is 76.33°, and similarly, the other O–Ru–O bite angle is 76.88°; the *trans* N–Ru–Ru angle is 158.93° in complex **1**. Two carbonyls are attached to each ruthenium atom bearing picolinate ligand. Overall two picolinate and eight carbonyl ligands are attached to three ruthenium atoms. Complex **1** has a glide plane perpendicular to [0, 1, 0] with glide component [1/2, 0, 1/2]. The order of the glide plane is 2. Perspective view of the glide planes is shown in the supporting information (Figure S1). The distance between two ruthenium atoms (Ru1 and

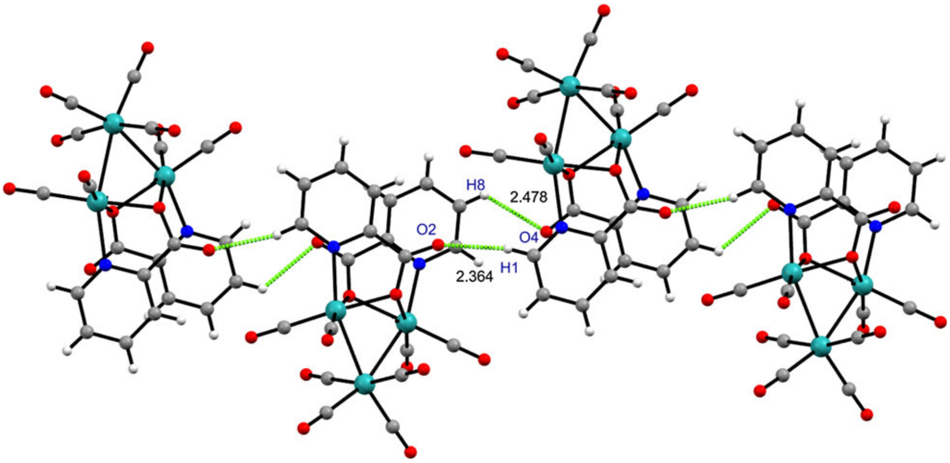
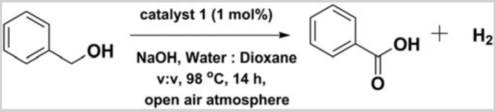


FIGURE 3 Hydrogen-bonded one-dimensional network in **1** along *c*-axis.

TABLE 3 Optimization for synthesis of benzoic acid from benzyl alcohol[a]



Entry	Solvent	Reaction atmosphere	Base (10 mmol)	Time (h)	Conv. (%)	Yield (%)	
						Benzoic acid	Hydrobenzoin
1	Dioxane	H_2O/Ar	NaOH	14	65	21	42
2	Methanol	H_2O/Ar	NaOH	14	19	19	0
3	Isopropanol	H_2O/Ar	NaOH	10	2	1	0
4	DMF	H_2O/Ar	NaOH	24	74	9	35
5	Chloroform	H_2O/Ar	NaOH	12	17	7	0
6	Acetonitrile	H_2O/Ar	NaOH	12	24	10	0
7	DMF	Ar	NaOH	24	7	0	0
8	Water	Ar	NaOH	12	0	0	0
9	Methanol	H_2O/O_2	NaOH	12	69	69	0
10	Ethanol	H_2O/O_2	NaOH	12	82	81	0
11	Isopropanol	H_2O/O_2	NaOH	12	90	90	0
12	*t*-Butanol	H_2O/O_2	NaOH	12	40	27	0
13	Isopropanol[b]	H_2O/O_2	NaOH	24	34	2	32

[a] Reaction conditions: benzyl alcohol (5 mmol), base (10 mmol), catalyst **1** (1 mol%), H_2O (500 μl), solvent (500 μl) were stirred at bath temperature of 98°C in an oil bath in open atmosphere. Products were analysed using GC-MS and ^1H NMR.

[b] Room temperature (25°C).

Ru2) is 3.068 Å which is more than that in the traditional $Ru_3(CO)_{12}$ crystal structure (2.848 Å).[37] Ru1 and Ru2 are bonded to Ru3 with bond lengths of 2.778 and 2.764 Å, respectively. The ruthenium atoms Ru1 and Ru2 are attached to two oxygen atoms sharing the electron pair, i.e. lone pair (2.207 Å) and bond pair (2.148 Å). Nitrogen donates its lone pair to Ru1 and Ru2 atoms with bond length of 2.514 Å.

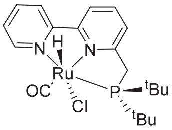
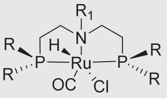
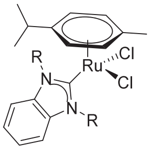
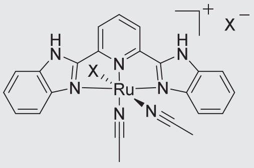
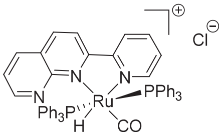
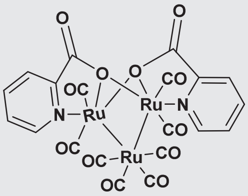
Complex **1** forms a one-dimensional polymeric chain using C—H···O interaction, i.e. H4···O5 with distance 2.705 Å, and H1···O2 and H8···O4 with distances of 2.364 and 2.478 Å, respectively (Figure 3). The one-dimensional chain extends to a two-dimensional network via π–π interaction between C6 and C10 with a distance of 3.354 Å (supporting information, Figure S2).

2.3 | Catalytic Experiments

The oxidation reaction of benzyl alcohol (Scheme 1) using 1 mol% of catalyst **1** was evaluated in water in the presence of various solvents between 75 and 100°C. Using dioxane or dimethylformamide (DMF) with water, a side product, hydrobenzoin, was obtained along with benzoic acid in inert (argon) atmosphere (Table 3, entries 1 and

TABLE 4 Comparative study of benzoic acid formation from benzylic alcohol using ruthenium complexes

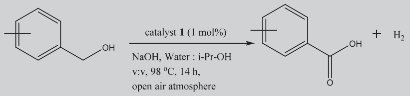
ruthenium complexes so far

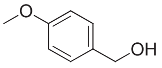
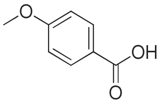
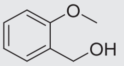
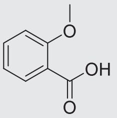
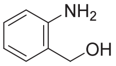
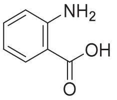
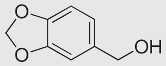
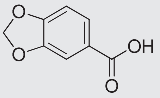
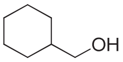
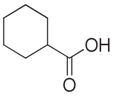
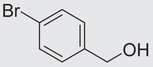
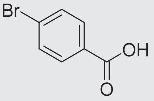
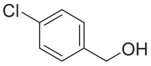
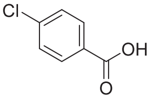
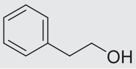
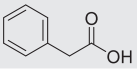
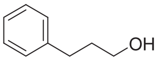
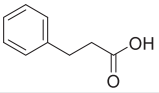
Entry	Catalyst or pre-catalyst	Substrate	Reaction parameters	Yield (%)	Ref.
1		Alcohol	Catalyst, NaOH, water (reflux), 18 h, argon	84	[30]
2	 R_1=H: R=Ph^{i}Pr R_1=CH_3: R=^{t}Bu R_1= H: R= Ph, ^{i}Pr	Alcohol	1) Catalyst, NaOH, 120°C, 20 h 2) Catalyst, KOH, 125°C, 20 h	1) 67 2) 92	[31,32,35]
3	 R=C_6H_{13}	Alcohol	Catalyst, NaOH, water (reflux), 24 h	92	[33]
4	 X=OTf	Benzyl alcohol	Catalyst, CsOH, water (reflux), 24 h (argon)	82	[34]
5		Benzyl alcohol	Catalyst, water, NaOH, 110°C, 6–24 h	100	[36]
6		Benzyl alcohol	Catalyst, NaOH, water, isopropanol, 98°C, 12 h	90	This work

4), whereas the same by-product was obtained at the lower temperature of standard condition (Table 3, entry 13). Using alcohols, chloroform and acetonitrile with water in inert atmosphere gave only benzoic acid, but in lower yields (Table 3, entries 2, 3, 5, 6). Neat solvents like DMF and *t*-butanol gave a lower yield in inert and open environment, respectively (Table 3, entry 7 and Table S2, entry 1). Using neat water in an argon atmosphere, without any other solvent, and without base, the reaction did not give any oxidized product (Table 3, entry 8 and Table S2, entry 2, respectively) as catalyst **1** is not soluble in neat water. In general, when the reactions were performed either in water and alcohol medium (inert atmosphere) or neat alcohol medium in open atmosphere, both led to lower yield of product. In contrast, when the reaction was performed in isopropanol and water (1:1) as the medium in open air atmosphere, a higher yield (90%) of benzoic acid was observed at 98°C (Table 3, entry 11). This significant result proves the importance of cluster **1** in catalysing the reaction of alcohol to carboxylic acid in basic water in open atmosphere. Several alcohols along with water as reaction medium were also studied, with isopropanol appearing as the most suitable solvent for this reaction (Table 3, entries 10–13).

We evaluated various bases in the oxidation reaction, K_2CO_3, KOH and NaOH. The most efficient bases were found to be KOH and NaOH as they are effective for de-protonation in alcohol/solvent medium. Interestingly,

TABLE 5 Synthesis of carboxylic acid derivatives from alcohols[a]



Entry	Reactant	Product	Conversion (%)	Yield by GC-MS (%)[b]
1			70	66
2			43	41
3			90	34
4			75	71
5			20	19
6			95	25
7			98	65
8			44	34
9			54	34

[a] Reaction conditions: alcohol (5 mmol), NaOH (10 mmol), catalyst **1** (1 mol%) were heated in an open atmosphere at bath temperature of 98°C. The reaction time was 14 h. Derivatives of benzoic acid were obtained by 2 M HCl acid treatment of the reaction mixture. Products were analysed using GC-MS, ^1H NMR and ^{13}C NMR.

[b] Yields measured by GC-MS are the average of three reactions with ±5% error observed.

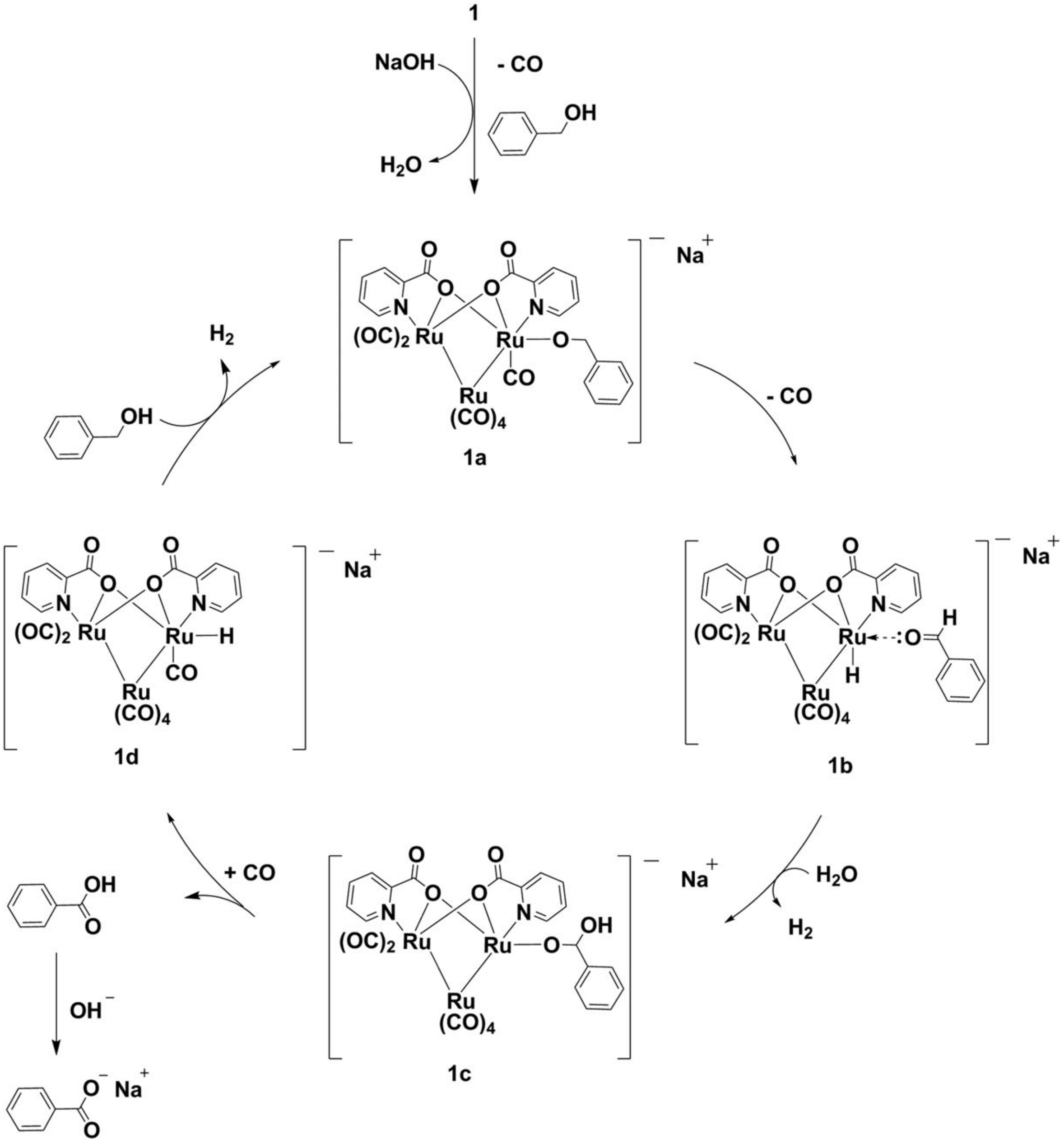


FIGURE 4 Plausible mechanism for catalytic oxidation of alcohol to carboxylic acid using ruthenium cluster [Ru3(CO)8(C5H4NCO2)2]. **NOTE: Editable chemdraw files are also attached in the next 2 pages**

at room temperature, hydrobenzoin was formed in high quantity and, as the temperature was increased (60°C), the formation of benzoic acid was enhanced. The optimization studies of temperature proved that the reaction was even possible at room temperature, 60 and 75°C but with lower conversion of benzyl alcohol to benzoic acid. This study proves that the catalyst **1** is also active even at lower temperature.

Previous examples of the synthesis of benzoic acid from alcohol as reported previously are summarized in Table 4. So far the reported catalysts (Table 4, entries 1–5) are either ruthenium hydride or ruthenium pincer complex precursors which require much effort and sensitive environment for their synthesis. In addition, the catalytic oxidation also needs a higher temperature. However, **1** is easily obtained by the simple chelation of picolinic acid ligand to $Ru_3(CO)_{12}$ by refluxing in toluene for an hour. Moreover, the reaction conditions for catalytic oxidation are also comparatively mild.

The substrate scope of the oxidation reaction is presented in Table 5. The catalytic oxidation is more favourable for substituents with electron-donating inductive effect (Table 5, entries 1 and 4). *Para*-substituted benzyl alcohols are more easily oxidized than *ortho*-

substituted benzyl alcohols likely because they are not creating any steric hindrance. The reaction was also performed with cyclic aliphatic compound; however, an inferior yield was obtained (Table 5, entry 5). The *p*-chloro-substituted benzyl alcohol gave a higher yield than *p*-bromo-substituted benzyl alcohol because of stronger C—Cl bond than C—Br bond, as benzoic acid is the other by-product along with *p*-halobenzoic acid. To prove the efficiency of catalyst **1** for aliphatic alcohol derivatives, 2-phenylethan-1-ol and 2-phenylpropan-1-ol were also explored and desired carboxylic acids were formed. So, the catalyst was also found to be active for aliphatic derivatives. Furthermore, when pyridyl ring-substituted compounds were used instead of benzyl substituents, the oxidation reaction did not occur, which is attributed to pyridine ring interaction with ruthenium and deactivation of catalyst **1**.

Several attempts were made to isolate the intermediate following various procedures[30,36,38,39] by reacting catalyst and benzyl alcohol in aqueous methanol as well as in $CHCl_3$. Unfortunately, the intermediate could not be isolated successfully. The role of the picolinic acid anion is most likely to assist removal of CO and subsequent addition of $PhCH_2O^-$ ligand.

The plausible oxidation mechanism is based on the Milstein mechanism for ruthenium(II) pincer catalyst[30] and here the catalytic transformation takes place at one of the Ru centres bridged by two picolinate ligands as $Ru_3(CO)_{12}$ itself does not catalyse the alcohol oxidation. After CO elimination, there follows the initial coordination of the deprotonated alcohol ($PhCH_2O^-$) to one of the two bridged Ru atoms (Figure 4, **1a**). This is followed, after CO de-coordination, by hydride beta-elimination from the Ru–OCH_2Ph species to give the coordinated aldehyde HRu(O═CHPh) (**1b**).[30,36] Further reaction with water gives a gem-diolate complex and H_2 elimination (**1c**). Beta-hydride elimination gives the final carboxylic acid product, and the RuH(CO) species (**1d**) is able to deprotonate $PhCH_2OH$ to give **1a**.

3 | CONCLUSIONS

In summary, a new $Ru_3(CO)_{12}$-based pyridine–acid cluster, $[Ru_3(CO)_8(C_5H_4NCO_2)_2]$, was synthesized by facile addition of picolinic acid to $Ru_3(CO)_{12}$, which was characterized using single-crystal X-ray diffraction. Complex/catalyst **1** was evaluated for the catalytic oxidation of alcohol to carboxylic acid (yield of 90%) using basic water in open atmosphere. The crystal structure of complex **1** revealed C—H⋯O and π–π interactions. Catalyst **1** is comparable with previously reported ruthenium hydride or ruthenium pincer complexes as it converts the primary alcohol to carboxylic acid at a relatively low temperature (98°C) in water in open environment (Scheme 1). Moreover, cluster **1** shows selectively high yield (90%) in water and isopropanol as the reaction medium. In the catalytic system, both water and oxygen (from the open atmosphere) take part in the oxidation of alcohol to carboxylic acid. These findings may open a route to the design of new clusters for the transformation of alcohols to corresponding carboxylic acid derivatives.

4 | EXPERIMENTAL

4.1 | Materials and Instrumentation

$Ru_3(CO)_{12}$, picolinic acid and alcohol derivatives were purchased from Aldrich and TCI Chemicals. Reagents used for purification and crystallization of products were purchased from Rankem and Merck and used as received. NMR spectra were recorded in $CDCl_3$ with a Bruker Avance (III) spectrometer (400 MHz). X-ray structural study of complex **1** was carried out using an Agilent Technologies Supernova CCD system. Samples were analysed using a Shimadzu QP2010 Ultra equipped with Rtx-5MS column (length 30 m, internal diameter 0.25 mm). The column oven programme was used as 40°C (hold 5 min) → 20°C min^{-1} → 280°C (hold 13 min) along with injection temperature of 280°C, interface temperature of 300°C and ion source temperature of 220°C.

4.2 | Single-Crystal X-ray Diffraction

A graphite-monochromated Cu Kα (λ_α = 1.54184 Å) source at 25°C was used to collect data. The standard phi–omega scan technique was used to collect data. The interpretation of the collected data was done using CrysAlisPro CCD software. The SHELXS-97 direct method was used to produce the crystal structures and refinement was done by the full-matrix least-squares method on F^2.[40] Olex-1.2 software was also used.[41] All the C—H⋯π interactions,[42] molecular drawings and mean plane analyses were obtained by Diamond (version 3.1d) and Mercury (version 3.1). The crystal structure and refinement data are shown in Figure 2 and presented in Table 4, respectively. And the bond distances and bond angles are presented in Table S1.

4.3 | Catalytic Reaction

Amounts of 5 mmol of benzyl alcohol and 10 mmol of NaOH were mixed with 500 μl of water and 500 μl of isopropanol solvent media. Catalyst **1** (1 mol%) was added. The reaction was performed at bath temperature of 98°C in the atmospheric oxygen environment. After 14 h, the solvent was evaporated and a white precipitate was observed. An amount of 5 ml of 2 M HCl was added to the reaction mixture and stirred for 5 min. Then 5 ml of ethyl acetate was added and extraction was done using ethyl acetate (5 × 3 ml). Then after brine wash, the recovered mixture was passed through a small column of sodium sulfate. After evaporation of the solvent, white solid benzoic acid was obtained. The solid was recrystallized using methanol and the NMR data show benzoic acid formation. The yield of benzoic acid was 90% which was similar to the result observed using GC-MS.

4.4 | Analysis of Products

After completion of reactions, the solvent was evaporated and products were isolated. Synthesized products were characterized using GC-MS, ^{1}H NMR and ^{13}C NMR. For more details, see supporting information (Figures S1–S35).

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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