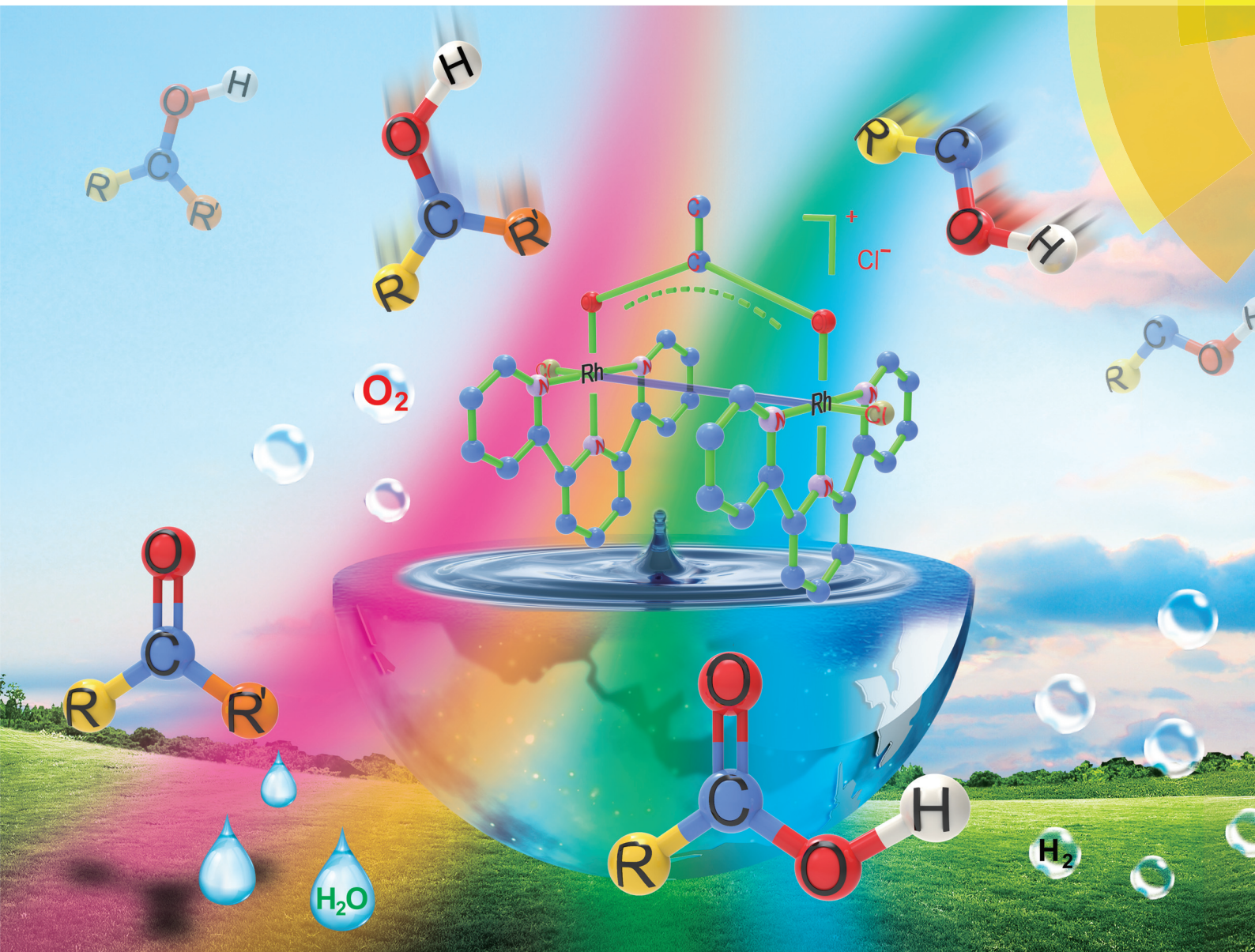


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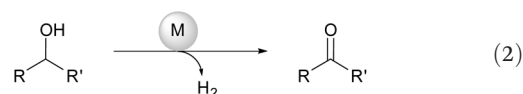
## Acceptorless dehydrogenation and aerobic oxidation of alcohols with a reusable binuclear rhodium(II) catalyst in water†

Xuwei Wang,<sup>a</sup> Chao Wang,<sup>\*a</sup> Yuxuan Liu<sup>a</sup> and Jianliang Xiao<sup>a,b</sup>

A water-soluble binuclear rhodium(II) complex was found to be an efficient catalyst for both acceptorless dehydrogenation and aerobic oxidation of alcohols under air to produce carboxylic acids or ketones in water. The catalyst is highly efficient with substrate/catalyst ratios up to  $5 \times 10^3$  being feasible, and could be recycled 19 times without significant loss of activity.

### Introduction

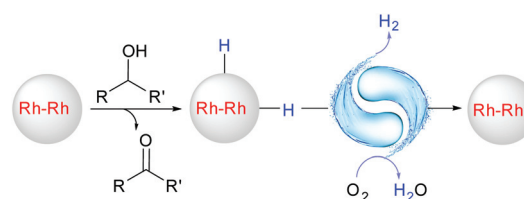
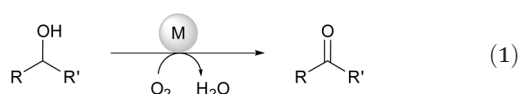
The oxidation of alcohols to their corresponding carbonyl compounds is one of the most important transformations in various chemical production processes.<sup>1</sup> Traditionally, stoichiometric quantities of inorganic<sup>2</sup> or organic<sup>3</sup> oxidants are employed to achieve this transformation. However, these reagents are often hazardous and generate stoichiometric amount of wastes. The use of molecular oxygen as an oxidant is a much more environmentally friendly choice.<sup>4</sup> The acceptorless dehydrogenation of alcohols is another green alternative, in which hydrogen gas is released as the only by-product which could be used as a fuel.<sup>5</sup> A range of catalysts have been developed to enable oxidation of alcohol *via* aerobic oxidation (eqn (1)) or acceptorless dehydrogenation (eqn (2)). Despite the progress made, we are unaware of a catalyst which is able to catalyse the oxidation of alcohols *via* both aerobic oxidation and acceptorless dehydrogenation. Such a catalyst is desirable, as it would allow one to choose an oxidation mode to suit the



reaction conditions and substrate compatibility. The difficulty to access catalysts of this ability lies in that catalysts that use  $\text{O}_2$  to drive the oxidation generally cannot evolve  $\text{H}_2$  whilst those that produce  $\text{H}_2$  are usually not stable in  $\text{O}_2$ .<sup>4,5</sup>

Most of the alcohol oxidation catalysts reported are mono-nuclear metal compounds.<sup>4–6</sup> In contrast, many oxidative enzymes contain binuclear metal centers as active sites.<sup>7</sup> Binuclear metal complexes may offer unique reactivity or selectivity patterns for catalysis.<sup>8</sup> In particular, binuclear Rh(II) complexes have been well studied.<sup>9</sup> However, none of them are known to catalyse aerobic or acceptorless dehydrogenation of alcohols.<sup>6e,9b,c,10</sup> Herein, we disclose that a binuclear Rh-tpy (tpy = 2,2':6',2''-terpyridine) complex<sup>11</sup> catalyses both acceptorless dehydrogenation and aerobic oxidation of alcohols (Scheme 1), producing carboxylic acids from primary alcohols and ketones from secondary alcohols. Moreover, the complex is water-soluble, allowing pure water to be used as a solvent. A substrate/catalyst (S/C) ratio of up to  $5 \times 10^3$  could be achieved and the catalyst could be reused up to 19 times without significant loss of activity under aerobic conditions.

Aqueous oxidation with soluble homogeneous catalysts is appealing, as it is not only environmentally benign but also offers the possibility for catalyst recycling.<sup>12</sup> Homogeneous



**Scheme 1** A binuclear rhodium catalyst capable of both acceptorless dehydrogenation and aerobic oxidation of alcohols in water.

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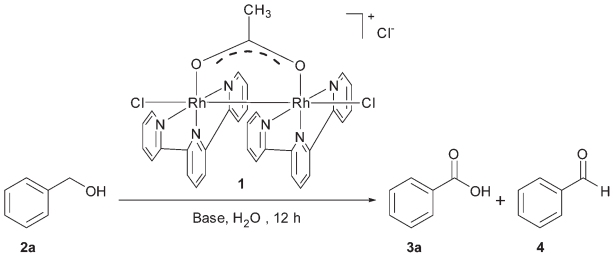
†Electronic supplementary information (ESI) available: Experimental procedures, characterisation data. See DOI: 10.1039/c6gc01272h



aqueous catalytic systems for aerobic oxidation of alcohols were reported by Sheldon,<sup>4c,13</sup> Buffin,<sup>14</sup> Komiya,<sup>6d</sup> Grützmacher,<sup>15</sup> Fu<sup>16</sup> and their co-workers. However, examples of acceptorless dehydrogenation of alcohols in water are few. Fujita,<sup>17</sup> Fukuzumi<sup>18</sup> and their co-workers reported water-soluble iridium catalysts for acceptorless dehydrogenation of alcohols to aldehyde or ketones, while Milstein and co-workers reported the first example of formation of carboxylic acids from alcohols with water as the oxygen source *via* acceptorless dehydrogenation with a Ru-PNN complex.<sup>19</sup> Recently, Ru-PNP complexes, a NHC-Ru catalyst and a heterogeneous Rh/C catalyst were found to be effective for the transformation of primary alcohols to carboxylic acids in water with the evolution of H<sub>2</sub>.<sup>20</sup> The recyclability of these catalysts has not been studied in most cases.<sup>6d,17,20d</sup>

## Results and discussion

During our efforts to develop acceptorless dehydrogenation reactions,<sup>21</sup> the binuclear rhodium complex **1**<sup>11,21d</sup> was found to catalyse the dehydrogenation of benzyl alcohols. In a model reaction, **2a** was converted to a mixture of benzoic acid **3a** and benzaldehyde **4** with water as the solvent in the presence of a base at 100 °C under argon at a S/C ratio of 200 (Table 1, entries 1–4). A base was found to play a critical role in the reaction, with both its strength and quantity affecting the reaction rate and chemoselectivity (Table 1, entries 1–4 and 6, also see Table S1 in the ESI†). Thus, 1 equivalent of a strong base afforded **3a** in good yield and selectivity (Table 1, entry 4).

**Table 1** Binuclear rhodium complex **1** catalysed oxidation of benzylalcohol<sup>a</sup>



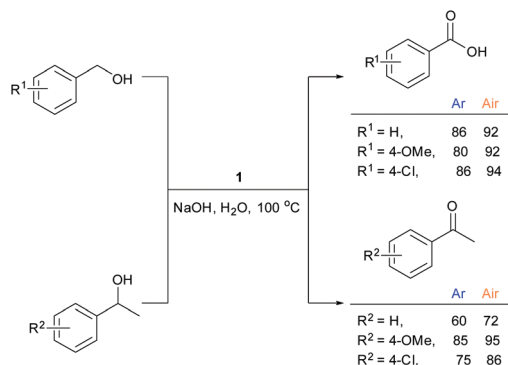
Entry	Base	Yield of <b>3a</b> <sup>b</sup> (%)		Yield of <b>4</b> <sup>b</sup> (%)
1	NaOAc	18		53
2	Na <sub>2</sub> CO <sub>3</sub>	68		23
3	NaHCO <sub>3</sub>	50	Under Ar	18
4	NaOH	86		<5
5 <sup>c</sup>	NaOH	94		<5
6 <sup>d</sup>	None	0		22
7 <sup>e</sup>	NaOH	0	Under air	<5

<sup>a</sup> Reaction conditions: **2a** (0.5 mmol), catalyst **1** (0.0025 mmol), base (0.5 mmol), H<sub>2</sub>O (2 mL), 100 °C, 12 h, under argon (Ar). <sup>b</sup> The yields were determined by GC with biphenyl as the internal standard. <sup>c</sup> Under air. <sup>d</sup> Without base under air. <sup>e</sup> Without catalyst under air.

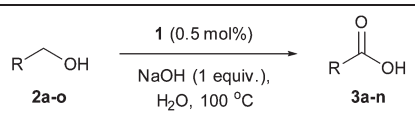
Further study revealed, interestingly, that performing the reaction under air afforded a higher yield of **3a** (Table 1, entry 5), and brought about a dramatic colour change from deep blue to orange (Table 1). This latter observation indicates a change in the reaction mechanism or in the resting state of the catalyst. Background reactions show that **1** and a base are both indispensable for the oxidation to carboxylic acid (Table 1, entries 6 and 7). Other Rh complexes, such as RhCl<sub>3</sub>·3H<sub>2</sub>O, [Rh(OAc)<sub>2</sub>]<sub>2</sub> and [Cp\*RhCl<sub>2</sub>]<sub>2</sub>, all showed poorer activities or selectivities than complex **1** under both argon and air (see Table S1 in the ESI†).

Preliminary examination of the substrate scope shows that both electron-rich and -deficient alcohols could be oxidised by **1** under either argon or air conditions (Scheme 2). Primary alcohols afforded carboxylic acids whilst the secondary ones led to ketones. Although bases alone were reported to promote aerobic oxidation of secondary alcohols to ketones,<sup>22</sup> stirring 1-(4-methoxyphenyl)ethanol with 1 or 2 equivalent of NaOH at 100 °C for 24 h in water under air afforded no observable ketone product, suggesting that a catalyst is essential for the oxidation.

The reactions under air are generally faster (Scheme 2) and operationally simpler than under argon. Thus, the substrate scope was further examined under air and the results for aromatic primary alcohols are summarised in Table 2. Substrates with electron-donating substituents are generally more reactive than the ones with electron-withdrawing substituents (Table 2, entries 2, 4–7 *vs.* entries 8–11). For the latter, higher catalyst loading, longer reaction time and an oxygen atmosphere were used (Table 2, entries 8–11). The cyano group and ester group were hydrolysable under the reaction conditions. Thus, the same product, terephthalic acid (**3j**), was obtained from both substrates **2j** and **2k** (Table 2, entries 10 and 11). Substituents at the *ortho*-position of the phenyl ring were tolerated (Table 2, entries 2 and 7). Unexpectedly, a *meta*-substituted substrate afforded poor yield under the standard conditions (Table 2, entry 3). Alcohols with oxygen-, sulphur- and nitrogen-containing heterocycles are viable substrates, affording their



**Scheme 2** 1-Catalysed oxidation of alcohols under both argon (Ar) and air. Numbers under Ar and Air denote yields (%). Reaction conditions: alcohols (0.5 mmol), catalyst **1** (0.0025 mmol), NaOH (0.005–1 mmol), H<sub>2</sub>O (2 mL), 100 °C, 8–20 h, isolated yields.

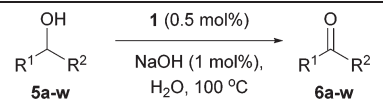
**Table 2** Oxidation of primary alcohols to carboxylic acid in water<sup>a</sup>


Entry	R	Product	Yield <sup>b</sup> (%)
1	Ph	<b>3a</b>	92
2	2-MePh	<b>3b</b>	93
3	3-MePh	<b>3c</b>	57
4	4-MePh	<b>3d</b>	87
5	2-OMePh	<b>3e</b>	89
6	4-OMePh	<b>3f</b>	92
7	2,4,5-OMePh	<b>3g</b>	96
8 <sup>c</sup>	4-ClPh	<b>3h</b>	95
9 <sup>c</sup>	4-FPh	<b>3i</b>	90
10 <sup>c</sup>	4-CNPh	<b>3j</b>	87
11 <sup>c</sup>	4-COOMePh	<b>3j</b>	90
12 <sup>c</sup>	Piperonyl	<b>3k</b>	90
13 <sup>c</sup>	2-Furyl	<b>3l</b>	86
14 <sup>c</sup>	2-Thienyl	<b>3m</b>	94
15 <sup>c</sup>	2-Pyridyl	<b>3n</b>	89

<sup>a</sup> Reaction conditions: alcohols (0.5 mmol), catalyst **1** (0.0025 mmol), NaOH (0.5 mmol), H<sub>2</sub>O (2 mL), 100 °C, 12 h, under air. <sup>b</sup> Isolated yields. <sup>c</sup> 1 mol% of **1**, 1 mol of NaOH, 20 h, under O<sub>2</sub>.

corresponding carboxylic acids in good yields (Table 2, entries 12–15).

The oxidation of secondary alcohols produces ketones and the results are summarised in Table 3. Secondary alcohols

**Table 3** Oxidation of secondary alcohols to ketones in water<sup>a</sup>


<b>6a</b> , R = Ph, 8 h, 72 (99)	<b>6i</b> , R = 4-ClPh, 8 h, 86 (99)
<b>6b</b> , R = 2-MePh, 8 h, 21 (25)	<b>6j</b> , R = 4-BrPh, 16 h, 51 (55)
<b>6c</b> , R = 3-MePh, 8 h, 90 (99)	<b>6k</b> , R = 4-CO <sub>2</sub> HPh, 16 h, 95 (99) <sup>b,c</sup>
<b>6d</b> , R = 4-MePh, 8 h, 85 (99)	<b>6l</b> , R = 4-CF <sub>3</sub> Ph, 16 h, 85 (99) <sup>b</sup>
<b>6e</b> , R = 4-OMePh, 8 h, 95 (99)	<b>6m</b> , R = 2-Furyl, 16 h, 82 (88)
<b>6f</b> , R = 3,4-OMePh, 8 h, 96 (99)	<b>6n</b> , R = 2-Thienyl, 16 h, 76 (82)
<b>6g</b> , R = 2-Naphthyl, 8 h, 94 (99)	<b>6o</b> , R = 2-Pyridyl, 16 h, 83 (92) <sup>b</sup>
<b>6h</b> , R = 4-FPh, 16 h, 75 (90)	

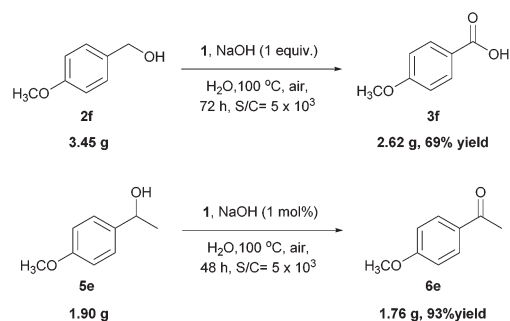
  

<b>6p</b> , 16 h, 95 (99)	<b>6q</b> , 16 h, 86 (99) <sup>b</sup>	<b>6r</b> , 16 h, 86 (99)	<b>6s</b> , 16 h, 95 (99)
<b>6t</b> , 16 h, 95 (99)	<b>6u</b> , 16 h, 96 (99)	<b>6v</b> , 16 h, 84 (99)	<b>6w</b> , 16 h, 90 <sup>b</sup>

<sup>a</sup> Reaction conditions: alcohol (0.5 mmol), catalyst **1** (0.0025 mmol), NaOH (0.005 mmol), H<sub>2</sub>O (2 mL), 100 °C, under air. Isolated yields (%) and conversions (%), numbers in brackets) are given. Conversions were determined by GC (**6a**, **6w**) or <sup>1</sup>H NMR (entries **6b–6v**) with 1,3,5-trimethoxybenzene as the internal standard. <sup>b</sup> With 0.5 mmol of NaOH. <sup>c</sup> With 4-(1-hydroxyethyl)benzotrionitrile as the substrate.

generally showed higher activities and only 1 mol% of NaOH is sufficient for most of their oxidation. Thus, 1-phenylethan-1-ol was fully converted to acetophenone in 8 h with 0.5 mol % of **1** and 1 mol% of NaOH at 100 °C. The isolated yield of 72% was lower than expected, probably due to the evaporation of acetophenone during the isolation process (Table 3, **6a**). The effect of installation of substituents on the phenyl ring of 1-phenylethan-1-ol was examined. Substrates with electron-donating substituents generally showed higher activities than the ones with electron-withdrawing groups (Table 3, **6c–6f** vs. **6h–6l**), with the latter ones requiring longer reaction time or the addition of 1 equivalent of NaOH. Poor yield was observed for the 4-Br substituted substrate due to unknown reasons (**6j**). A substituent at the *ortho*-position of the phenyl ring exerted a strong influence on the alcohol reactivity. Thus, only 25% of conversion was observed for 1-(*o*-tolyl)ethan-1-ol (**6b**). A good yield was obtained for 1-(naphthalen-2-yl)ethan-1-ol (**6g**). Heterocycle-containing secondary alcohols were suitable substrates, albeit with lower reactivity (Table 3, **6m–6o**). Replacing the methyl group of 1-phenylethan-1-ol with other alkyl substituents (*e.g.* *n*-propyl, *i*-propyl and cyclopropyl, Table 3, **6p–6r**) or with phenyl groups (Table 3, **6t**, **6u**) did not affect the high yields obtained. 1-Indanol was oxidised to 1-indanone in a yield of 95% (**6s**). Notably, the C=C double bond of an allylic alcohol was intact, which was oxidised to an  $\alpha,\beta$ -unsaturated ketone (**6v**). An example of aliphatic alcohol oxidation is seen in cyclohexanol, which afforded cyclohexanone (**6w**).

Since **1** is water-soluble, the product/catalyst separation was straightforward in all the reactions above, requiring a simple phase separation (see the ESI<sup>†</sup>). To showcase the practical usefulness of the catalytic system, gram scale reactions with high S/C ratios were carried out (Scheme 3). At a S/C ratio of 5000, 3.45 g of **2f** was converted to 2.62 g of 4-methoxybenzoic acid **3f** (69% yield), obtained after acidification followed by filtration. Similarly, 1.9 g of **5e** was oxidised to 1.76 g of 1-(4-methoxyphenyl)ethan-1-one **6e** (93% yield), with the product abstracted with petroleum ether from water. ICP-MS analysis of the products showed that only a trace amount of rhodium was leached (9.8 ppb in **3f**; 4.7 ppb in **6e**). This would make

**Scheme 3** Gram scale reactions catalysed by **1** in water. See the ESI<sup>†</sup> for details.

this protocol suitable for synthetic tasks with the most stringent control on residual metal levels.

The high water solubility of **1** also offers the possibility for easy catalyst recycle. This is demonstrated in the oxidation of 1-(4-methoxyphenyl)ethanol to **6e** (Fig. 1). After a catalytic reaction, the product was extracted with petroleum ether. The catalyst **1** remained in the aqueous phase, which could be reused for the oxidation of a freshly added substrate. As illustrated in Fig. 1, the catalyst was recycled 20 times this way, with its activity having decreased only insignificantly in the first 19 runs. To the best of our knowledge, this is the highest recycle numbers ever achieved for the aerobic oxidation of alcohols in water.<sup>17</sup>

Preliminary mechanistic studies were carried out to shed light on the mechanism of **1** catalysed oxidation. Hydrogen gas was detected by GC from the head gas of **1**-catalysed oxidation of 1-phenylethanol under argon, whilst no hydrogen gas was observed when the reaction was carried out with an air balloon. The quantitative measurement of the hydrogen gas released under a nitrogen atmosphere indicates that 1 equivalent of hydrogen gas was produced for the oxidation of secondary alcohols to ketones (see section 7.4 of the ESI† for details). Moreover, when the reaction was carried out under air in a sealed Radleys reaction tube, the oxygen in the tube was completely consumed by GC analysis of the head gas after the reaction, and hydrogen gas was detected (see the ESI† for details), which indicates that the reaction in the sealed tube switched from aerobic oxidation to acceptorless dehydrogenation after the oxygen in the tube was consumed. These results suggest that the reaction under argon proceeds *via* an acceptorless dehydrogenation pathway, giving off H<sub>2</sub>, while under air, oxygen acts as the terminal oxidant, converting the hydrogen to water (Scheme 1).

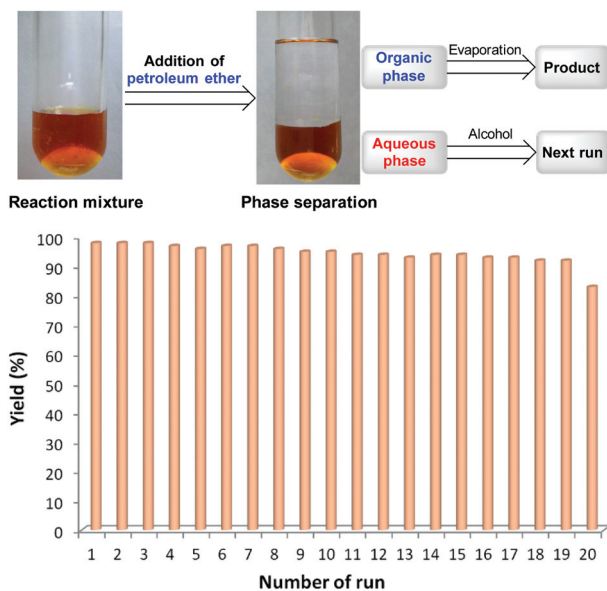
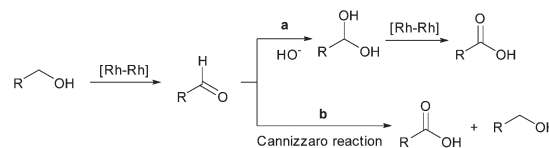


Fig. 1 Reuse of the catalyst **1** in the oxidation of **5e** in water. See the ESI† for detailed reaction conditions.



Scheme 4 Possible pathways for the formation of carboxylic acids from primary alcohols.

For the oxidation of primary alcohols to carboxylic acids, there are two possible pathways following the initial formation of an aldehyde, which was detected during the reaction: (a) attack of the aldehyde by the base to form a hemiacetal intermediate, which is then dehydrogenated by the catalyst to produce the carboxylic acid; (b) the aldehyde undergoes a base-promoted Cannizzaro reaction to afford the carboxylic acid and the starting alcohol, which could be oxidised to the aldehyde again. Experiments were designed to probe which pathway the reaction might take (see the ESI† for details). The experiments showed that the Cannizzaro reaction of an aldehyde under basic conditions was very slow and complex **1** accelerated the oxidation of aldehydes to carboxylic acids, suggesting that the reaction proceeds mainly *via* the pathway a as shown in Scheme 4, where the catalyst catalyses both steps of the oxidation. The carboxylic acid could be formed under both argon and air atmosphere, which suggests that the newly introduced oxygen in the carboxylic acid might come from NaOH or water for both cases and the role of oxygen might be to remove the hydrogens from alcohol to form water.

## Conclusions

In conclusion, a water-soluble binuclear rhodium(II) complex has been identified to be an efficient catalyst for the oxidation of alcohols to carboxylic acids or ketones in water *via* either acceptorless dehydrogenation or aerobic oxidation with air. The catalyst could be removed from the product by simple phase separation and reused 19 times without significant loss of catalytic activity. Being easy to operate and scale up and of broad substrate scope, the reaction provides a practical and green method for the oxidation of alcohols. The detailed mechanism and further application for the binuclear Rh(II) complex catalysed acceptorless dehydrogenation and aerobic oxidation are under investigation in our laboratory.

## Acknowledgements

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