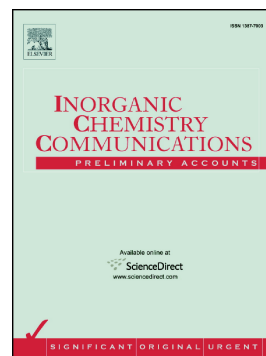


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Efficient selective oxidation of alcohols to carbonyl compounds catalyzed by Ru-terpyridine complexes with molecular oxygen

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Abstract: The oxidation of alcohols with molecular oxygen is a promising approach to produce corresponding carbonyl compounds. In this work, efficient aerobic oxidation of alcohols to carbonyl compounds catalyzed by ruthenium-terpyridine [(tpy-PhCH₃)RuCl₃] with isobutyraldehyde as co-substrate was developed. Various alcohols including primary and secondary alcohols are smoothly converted to corresponding carbonyl compounds in good yield. In a 100 times large-scale oxidation of benzyl alcohol, benzaldehyde was obtained with 92% isolated yield. Moreover, a plausible mechanism involving high-valence ruthenium species was proposed based on *in situ* UV-vis spectroscopy.

Keywords: Alcohol oxidation; Carbonyl compounds; Ruthenium-terpyridine; Molecular oxygen; Mild conditions

Introduction

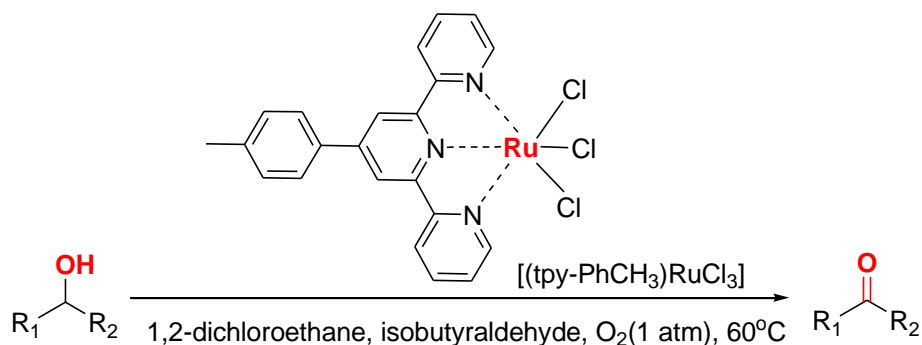
The selective oxidation of alcohols to corresponding carbonyl compounds is one of the most important processes because aldehydes or ketones is a fundamental transformation in organic synthesis [1-3]. Traditional methods for this selective oxidation involve the use of a stoichiometric amount of oxidants such as MnO₂ [4-6], chromium oxides [7], which produce a large amount of toxic waste. Due to the

growing concerns for environmental preservation and cost effective, catalytic oxidation processes with molecular oxygen or air are extremely valuable and particularly attractive [8]. A variety of methods reported in the literature for the aerobic oxidation of alcohols are based on metal catalysts such as manganese [9-11], cobalt [12-14], ruthenium [15-17] and Au nanoparticles or Au/CuO-hydroxyapatite [18-20] etc. Among these catalytic systems, based on nitroxyl radical like TEMPO and NHPI in combination with catalysts are the most reported [21-23].

Aldehyde acts as a reducing agent for the reductive activation of dioxygen is widely reported in the oxidation, in which the catalysts involved metalloporphyrins [24] and Mn salen complexes [25] etc. Rahimi *et al.* reported the effective alcohol oxidation in the presence of Cu(II) *meso*-tetraphenylporphyrin and isobutyraldehyde [26]. We ever reported an efficient oxidation process of alcohol catalyzed ruthenium tetraphenylporphyrins in the presence of molecular oxygen and isobutyraldehyde [27]. Recently, organic-inorganic hybrid cobalt phthalocyanine exhibited good activity for the selective oxidation of alcohol by using isobutyraldehyde as co-substrate [28].

Ruthenium complexes with nitrogen-based ligands such as pyridine have been intensively investigated in order to develop catalysts for organic oxidation processes. Nishiyama first reported the asymmetric epoxidation by one kind of ruthenium complex based on bis(oxazoliny)pyridine [29]. Although this kind ruthenium compounds were used in the oxidation of alcohol, hydrogen peroxide and TBHP (*tert*-butylhydrogen peroxide) were mostly used as oxidant [30]. The selective oxidation of alcohols catalyzed by ruthenium(II) complexes of pyridine ligand complexes with molecular oxygen as oxidant is still limited.

As part of our ongoing interests in green oxidations process with dioxygen, the aerobic oxidation of alcohols to carbonyl compounds catalyzed by ruthenium-terpyridine [(tpy-PhCH₃)RuCl₃] in the presence of isobutyraldehyde has been developed in this work (*Scheme 1*). The catalytic system has been proved to be efficient for oxidation of alcohols with high yields for carbonyl compounds under mild conditions.



Scheme 1 Aerobic oxidation of alcohols catalyzed by $[(\text{tpy-PhCH}_3)\text{RuCl}_3]$

2. Experimental

2.1 Reagents and methods

Different para-substituted alcohols, aldehydes and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ were purchased from Sigma. Other Chemicals were of analytical grade and purchased from Aldrich without further purification unless indicated. Solvents were of analytical purity and used as received. The precursor that used for the synthesis of the ligand 4'-(p-methylphenyl)-2,2':6',2''-terpyridine (tpy-PhCH₃) was synthesized following reported procedures [31]. $[(\text{tpy-PhCH}_3)\text{RuCl}_3]$ was prepared by refluxing $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and tpy-PhCH₃ (1:1 molar ratio) in EtOH according to the previous procedures [32].

Mass spectra were obtained on a Shimadzu LCMS-2010A. Elemental analyses were carried out with an Elementar vario EL elemental analyzer. ¹H NMR was recorded on a Bruker AVANCE 400 spectrometer (500MHz). IR spectra were recorded on a Bruker 550 FT-IR spectrometer. UV spectra were recorded on a Shimadzu UV-2450 spectrophotometer. The *in situ* UV-vis spectra of ruthenium complex were recorded on the AvaSpec-2048 spectrometer, which was equipped with a high-pressure, high-temperature probe and connected to the stainless-steel reactor.

The structure characterization data of $[(\text{tpy-PhCH}_3)\text{RuCl}_3]$: ¹H NMR: (500MHz, CDCl₃): δ 10.59(s, 2H), 10.46 (m, 4H), 9.66 (s, 2H), 9.37(m, 2H), 9.13 (m, 4H), 3.98 (m, 3H). IR (KBr)/cm⁻¹: 3032, 1620, 1473, 1093, 820, 784. UV-vis, CH₃CN, λ_{max} nm(logε): 205(0.31), 286(0.18), 514(0.05). EI-MS: *m/z*=530. Elemental analysis Calcd(%). for C₂₂H₁₇Cl₃N₃Ru: C, 49.76; H, 3.23; N, 7.92. Found: C, 48.61; H, 3.51; N, 7.43.

2.2 Catalytic oxidation of alcohol

The catalytic oxidation of alcohol was carried out in a magnetically stirred glass reaction tube fitted with a reflux condenser. A typical procedure was as follows using benzyl alcohol as a model substrate: A solution of 1,2-dichloroethane (DCE, 5 mL), benzyl alcohol (1 mmol), isobutyraldehyde (2 mmol), [(tpy-PhCH₃)RuCl₃] (1×10^{-3} mmol, 0.1 mol% based substrate) and 0.5 mmol naphthalene (inert internal standard) were added in the tube. Then the mixture was stirred at 60°C for 60 min under dioxygen balloon. The consumption of the starting alcohols and formation of products were monitored by GC and GC-MS. GC analyses were performed on a Shimadzu GC-2010 plus chromatography equipped with Rtx-5 capillary column (30m×0.25mm×0.25μm). GC-MS analyses were recorded on a Shimadzu GCMS-QP2010 equipped with Rxi-5ms capillary column (30m×0.25 mm×0.25μm).

3. Results and discussion

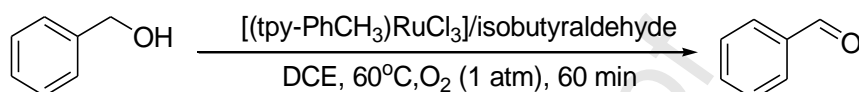
3.1 Alcohol oxidation under different conditions

By using benzyl alcohol as the model substrate, the reaction conditions were optimized with [(tpy-PhCH₃)RuCl₃] as the catalyst. As shown in Table 1, In control experiments without the catalyst, only 13% benzyl alcohol was converted (entry 1 in Table 1). As the oxidation was conducted in the absence of isobutyraldehyde as co-substrate, no yield of benzaldehyde was obtained (entry 2 in Table 1). This results also indicate that isobutyraldehyde plays a significant role in the oxidation of benzyl alcohol. Higher yield of benzaldehyde could be obtained with the usage of isobutyraldehyde increasing (entries 3~7 in Table 1). However, no significant difference was observed when the amount of isobutyraldehyde reached up to 2 equiv. for the present system.

In addition, the role of isobutyraldehyde is to activate dioxygen through free radical chains propagation in the catalytic system [33]. As another kind of aldehyde, the oxidation product benzaldehyde maybe also promote the catalytic efficiency. However, almost no oxidation occurred when benzaldehyde was used as co-substrate (entry 8 in Table 1). Hence, the possible that benzaldehyde participated in the

oxidation could be excluded. Moreover, from the viewpoint of cost-effective, catalytic oxidation with air is extremely valuable and attractive for industrialization. When the oxidation was conducted under atmospheric pressure air, 52% yield of benzaldehyde was obtained (entry 9 in Table 1). But the catalytic efficiency was remarkably enhanced when the air was pressured to 1.0 MPa (entry 10 in Table 3).

Table 1. Aerobic oxidation of benzyl alcohol catalyzed by [(tpy-PhCH₃)RuCl₃] with isobutyraldehyde^a



Entry	Catalyst	isobutyraldehyde (equiv.)	Conv. (%)	Select. (%)
1	-	2.0	13	>99
2	[(tpy-PhCH ₃)RuCl ₃]	-	<1	-
3	[(tpy-PhCH ₃)RuCl ₃]	0.5	51	>99
4	[(tpy-PhCH ₃)RuCl ₃]	1.0	73	>99
5	[(tpy-PhCH ₃)RuCl ₃]	1.5	87	>99
6	[(tpy-PhCH ₃)RuCl ₃]	2.0	99	>99
7	[(tpy-PhCH ₃)RuCl ₃]	3.0	99	>99
8 ^b	[(tpy-PhCH ₃)RuCl ₃]	-	3	>99
9 ^c	[(tpy-PhCH ₃)RuCl ₃]	2.0	52	>99
10 ^d	[(tpy-PhCH ₃)RuCl ₃]	2.0	96	>99

^a Benzyl alcohol (1mmol), [(tpy-PhCH₃)RuCl₃] catalyst (0.1 mol%), DCE (5 mL), 60°C, 60 min, under O₂ balloon.

^b Benzaldehyde (2 mmol) was used as co-substrate.

^c Atmospheric air as oxidant.

^d Air as oxidant, air pressure was 1.0 MPa.

Aerobic oxidation of benzyl alcohol with [(tpy-PhCH₃)RuCl₃] catalyst using various solvents and the effect of reaction temperature on its conversion were also investigated and the results were summarized in Table 2.

Table 2. Effect of solvent and temperature on the oxidation of benzyl alcohol^a

Entry	Solvent	T (°C)	Conv. (%)	Select. (%) ^b
-------	---------	--------	-----------	--------------------------

1	Cyclohexane	60	83	>99
2	Toluene	60	86	>99
3	1,2-Dichloroethane	60	99	>99
4	Ethyl acetate	60	51	87(13)
5	Acetonitrile	60	35	90(10)
6	Methanol	60	26	78(22)
7	1,2-Dichloroethane	40	46	>99
8	1,2-Dichloroethane	50	72	>99
9	1,2-Dichloroethane	70	>99	>99

^aBenzyl alcohol (1mmol), [(tpy-PhCH₃)RuCl₃] (0.1 mol%), isobutyraldehyde (2 equiv.), solvent (5 mL), 60°C, 60 min, under O₂ balloon.

^bThe numbers in parentheses indicate the selectivity of benzoic acid.

It seems that the solvent plays a key role in the oxidation system. Compared with cyclohexane and toluene, DCE (1,2-dichloroethane) was more favorable to the oxidation of benzyl alcohol, which gave 99% yield of benzaldehyde (entries 1~3 in Table 2). When stronger polarity solvents such as ethyl acetate, acetonitrile, and methanol were used instead, the significantly declined efficiency could be obtained, companies with the formation of benzoic acid (entries 4~6 in Table 2).

The effect of temperature on oxidation of benzyl alcohol was also investigated. The conversion was increased with raising the temperature from 40°C to 70°C (entries 7~9 in Table 2). It is notable that the increasing temperature could hardly influence the selectivity towards benzaldehyde, *i.e.*, no over-oxidation product such as benzoic acid was observed.

Subsequently, the catalyst amount was examined for the selective oxidation of benzyl alcohol. As shown in Figure 1, lower catalysts usage present less efficient under the standard reaction conditions. The yield of benzaldehyde increased with the rising amount of catalyst. But no significant difference in efficiency was observed when the amount of catalyst was increased up to 1.0 mol% (based on the substrate).

However, an excess amount of catalyst caused a decrease of selectivity towards benzaldehyde, which resulted in the over-oxidation to generate by-product benzoic acid.

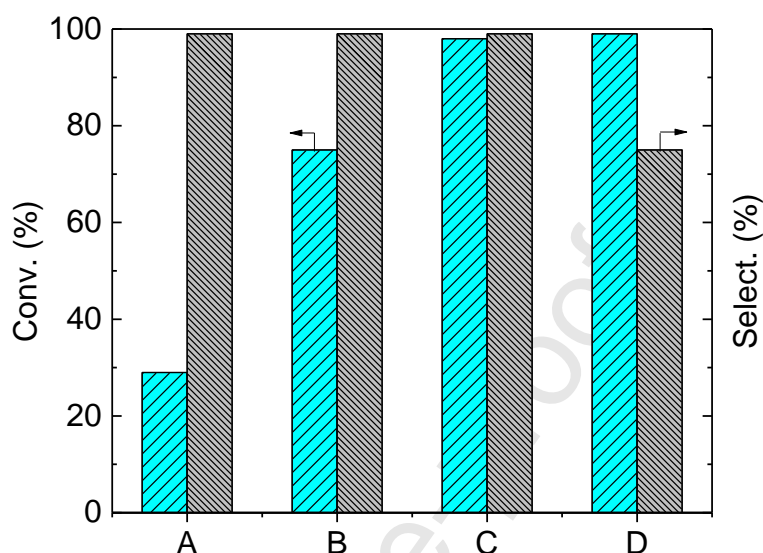


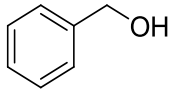
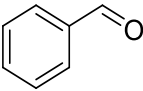
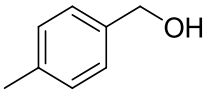
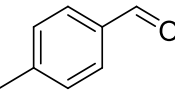
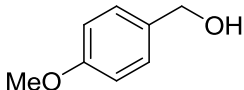
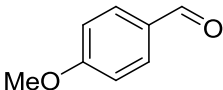
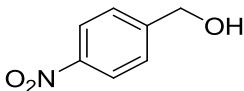
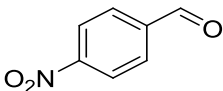
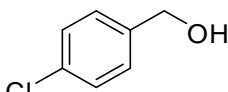
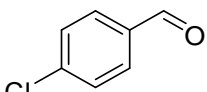
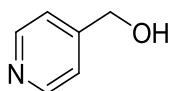
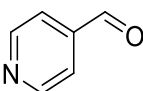
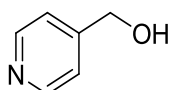
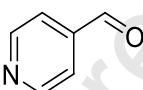
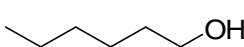

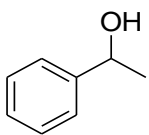
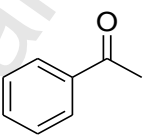
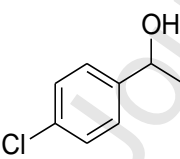
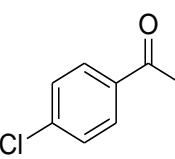
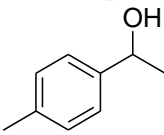
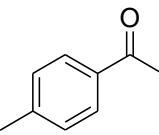
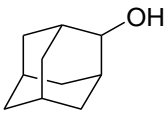
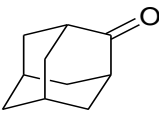
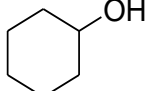
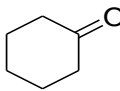
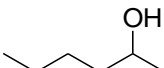
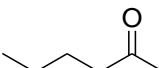
Figure 1. Effect of catalyst amount on benzyl alcohol oxidation (A: 0.001 mol%; B: 0.01 mol%; C: 0.1 mol%; D: 1.0 mol%). Benzyl alcohol (1mmol), [(tpy-PhCH₃)RuCl₃], isobutyraldehyde (2 equiv.), DCE (5 mL), 60°C, 60 min, O₂ balloon.

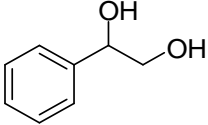
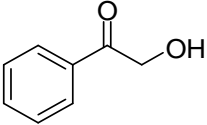
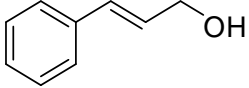
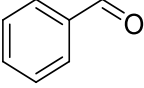
3.2 Aerobic oxidation of other alcohols by [(tpy-PhCH₃)RuCl₃]

To evaluate the scope of the catalytic system, oxidation of various alcohols, including benzylic alcohols, secondary alcohols, and primary alcohols, by dioxygen in the presence of [(tpy-PhCH₃)RuCl₃] under mild conditions has been investigated (Table 3).

Table 3. Oxidation of various alcohols with dioxygen catalyzed by [(tpy-PhCH₃)RuCl₃]^a

Entry	Substrate	Product	Time/min	Conv./%	Selectc./%
-------	-----------	---------	----------	---------	------------

1			60	98	>99
2			60	99	>99
3			60	99	>99
4			120	65	90
5			60	69	92
6			120	60	99
7 ^b			120	92	>99
8			60	99	>99
9			60	>99	>99
10			60	79	>99
11			60	98	>99
12			60	92	>99
13			60	>99	>99
14			60	97	>99

15 ^c			60	98	12(88)
16 ^d			60	>99	90(10)

^aSubstrate (1 mmol), [(tpy-PhCH₃)RuCl₃] (0.1 mol%), isobutyraldehyde (2 equiv.), DCE (5 mL), 60°C, O₂ balloon.

^b[(tpy-PhCH₃)RuCl₃] (0.2 mol%).

^cThe number in parentheses was the selectivity of benzaldehyde.

^dThe number in parentheses was the selectivity of cinnamaldehyde.

It could be known that the catalytic system was efficient for most primary alcohol, which alcohols were smoothly converted to corresponding carbonyl compounds with a high conversion and excellent selectivity (entries 1~8 in Table 3). It seems that the catalytic activity is dependent on the electronic property of substrates. The catalytic system was more effective for the substrates with electron-withdrawing groups at *para* position (entries 2-5 in Table 3). It was inefficient for basic substrates like 4-pyridinemethanol (entry 6 in Table 3), which only 60% conversion was obtained even prolonged reaction time to 120 min. However, the catalytic efficiency could be improved by increasing amount of catalyst for 4-pyridinemethanol (entry 7 in Table 3). The catalytic system is also efficient for the oxidation of saturated primary aliphatic alcohols such as 1-octanol (entry 8 in Table 3).

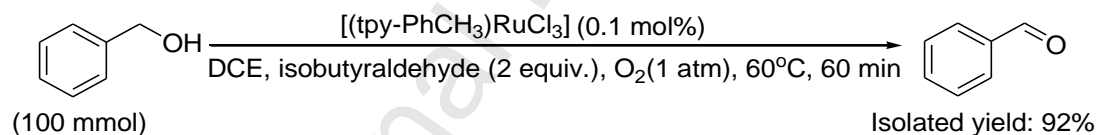
Secondary alcohols could be easily converted to the corresponding ketones in high yields (entries 9-14 in Table 3). The influence of the electronic property was confirmed further from the secondary alcohols oxidation (entries 10 and 11 in Table 3). The catalytic system also were apparently more conducive for the secondary alcohols with electron-withdrawing groups than that of electron-donating groups. As for 2-adamantanol, the catalytic system shows high activity, which gave ketone yield of 92% despite the hindrance (entry 12 in Table 3).

Furthermore, the catalytic system also exhibited high activity for the oxidation of diol, such as 1-phenyl-1,2-ethanediol (entry 15 in Table 3). The main product was benzaldehyde that resulted from the oxidative cleavage of C-C bonds. Diols could be

cleaved to the corresponding aldehydes by ruthenium porphyrins with molecular oxygen as oxidant [27]. Similar C=C bond cleavage could also be found when cinnamyl alcohol was carried out (entry 16 in Table 3). Cinnamyl alcohol could be converted completely and benzaldehyde was the main product. This phenomenon is similar to that of MnTPPCl-catalyzed aerobic oxidation of cinnamyl alcohol [34].

3.3 Large-scale oxidation of benzyl alcohol

To further confirm the practicality and efficiency of this catalytic system, a 100 times large-scale experiment for the oxidation of benzyl alcohol was conducted under standard conditions. The reaction solution mixture with dioxygen bubbling was stirred at 60 °C for 60 min. After removing of the solvent under reduced pressure, the crude products were purified *via* column chromatographic (silica gel, petroleum ether as eluting agent). Pure benzaldehyde was obtained with the yield of 92% by removing solvent (*Scheme 2*). The result suggested that this catalytic system was amenable to scale up.



Scheme 2. Large-scale oxidation of benzyl alcohol

3.4 Plausible mechanism

As reported previously, the activation of molecular oxygen by aldehyde in oxidation proceeded *via* a free radical process. In order to verify the free-radical mechanism, 2,6-*di-tert*-butylphenol serving as the free-radical inhibitor was used in the oxidation solution. After the addition of this inhibitor, the oxidation was subsequently quenched.

The ruthenium complexes catalyst was monitored by *in situ* UV-vis spectroscopy (AvaSpec-2048×14 with a fiber optic probe) during the reaction with isobutyraldehyde and dioxygen at 60 °C. Figure 2 shows an initial characteristic absorption peak of [(tpy-PhCH₃)RuCl₃] at 205 nm. Note that the spectrophotometer was programmed to acquire UV-vis spectra every 10 min. As the reaction proceeded,

the peak at 205 nm gradually decreased in intensity, accompanied by the increase of the peak at 228nm.

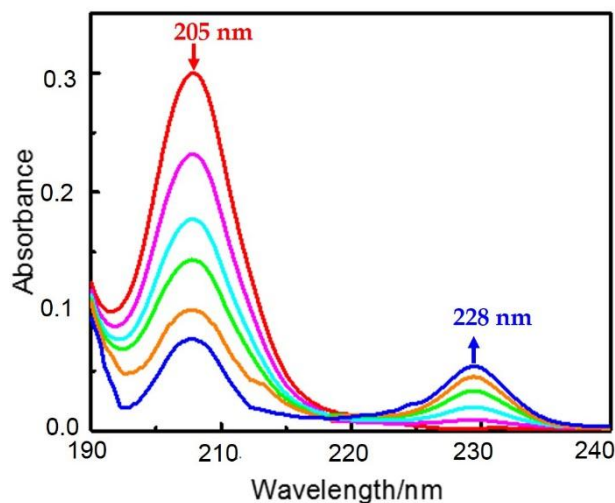
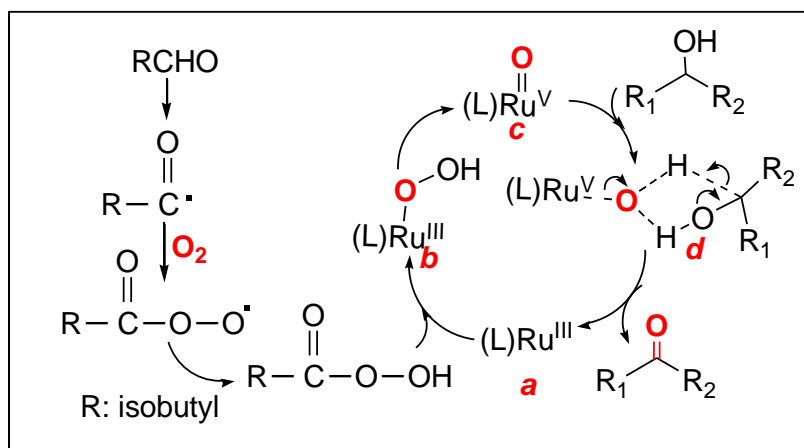


Figure 2. *In situ* UV-vis spectra of $[(\text{tpy-PhCH}_3)\text{RuCl}_3]$ catalyst during aerobic oxidation of benzyl alcohol in presence of isobutyraldehyde (interval 10 min), benzyl alcohol (10 mmol), catalyst (1×10^{-2} mmol), DCE (50 mL), isobutyraldehyde (2.0 equiv.) and 60°C .

This change was attributed to the generation of high-valent ruthenium complex during oxidation. The recorded spectroscopic features supported the conclusion that the complex was converted into ruthenium-oxo species [35]. As reported previously by Beller, ruthenium oxo complex was the active catalyst species in the asymmetric epoxidation system [36]. As to $[(\text{tpy-PhCH}_3)\text{RuCl}_3]$ in presence of isobutyraldehyde and O_2 , the reaction mechanism could also involve the participation of Ru-oxo species generated from the reaction between $[(\text{tpy-PhCH}_3)\text{RuCl}_3]$ and dioxygen through a series radical chain. The formation of carbonyl compounds was attributed to the reaction of the alcohol with Ru-oxo species, followed by β -hydride elimination.

Based on the above discussion, a plausible mechanism was proposed for the oxidation of benzyl alcohol catalyzed by $[(\text{tpy-PhCH}_3)\text{RuCl}_3]$ in presence of dioxygen and isobutyraldehyde, and it is shown in *Scheme 3*.



Scheme 3. Plausible mechanism of [(tpy-PhCH₃)RuCl₃]-catalyzed oxidation of alcohol in presence of isobutyraldehyde and molecular oxygen.

An acyl radical is derived from the thermal abstraction of hydrogen at the carbonyl position at first. Peroxyacid was generated by radical propagation. Then, the reaction should be initiated by the smooth interaction between Ru(III) complex (*a*) and peroxy acid to generate Ru(III)-OOH (*b*) [37-38]. Ru-oxo (*c*) was then generated from heterolytic cleavage of O-O bond of species (*b*). Due to the electrophilic character of Ru-oxo (*c*), the formation of carbonyl compounds was attributed to the reaction of the alcohol with Ru-oxo species through transition species (*d*), followed by β -hydride elimination.

4. Conclusions

In summary, ruthenium complex [(tpy-PhCH₃)RuCl₃] has been proven to be an excellent catalyst for oxidation of alcohols in the presence of molecular oxygen and isobutyraldehyde. The catalytic system exhibited excellent substrate tolerance, both primary and secondary alcohols were oxidized into their corresponding carbonyl compounds in good yield. The influence of various reaction parameters such as solvent, catalyst and oxidant amount on the activity and selectivity was evaluated. In a 100 times large-scale oxidation of benzyl alcohol, benzaldehyde was obtained with 92% isolated yield.

Acknowledgments

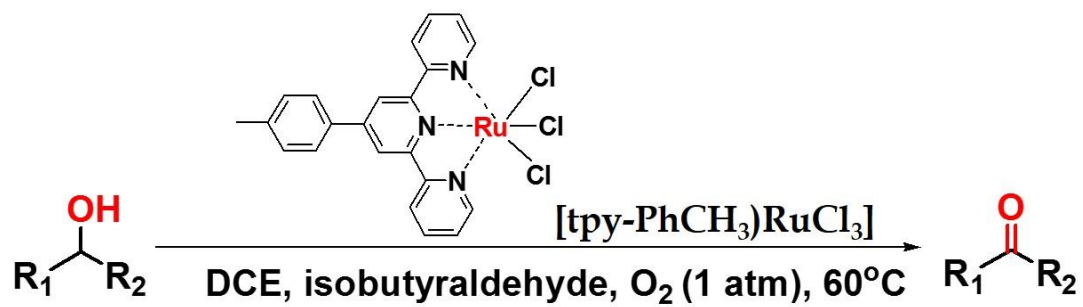
This study was supported by the National Key Research and Development Program of China (2016YFA0602900), the National Natural Science Foundation of China (No. 21576302, 21878344 and 21425627), Guangdong Technology Research Center for Synthesis and Separation of Thermosensitive Chemicals (2015B090903061) and Science and Technology Innovation Teams Project of Huizhou (20131226121851953).

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Graphical Abstract



- Mild reaction conditions
- Be amenable to scale up
- Broad substrate scope
- Dioxygen as oxidant

Journal Pre-proof

Highlights

- ▶ Ruthenium-terpyridine presented excellent efficiency for alcohol oxidation.
- ▶ Aerobic oxidation of alcohols were carried out under mild conditions.
- ▶ The catalytic protocol could be amenable to scale up.

Journal Pre-proof