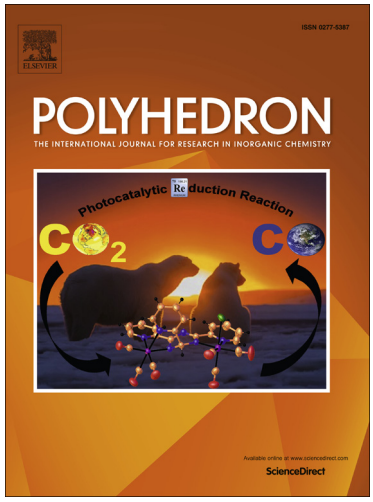

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Synthesis, single crystal structure and efficient catalysis for alcohol oxidation of a novel Ru(II) complex with both a N,N,N-tridentate ligand and a pyridinedicarboxylate

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Abstract: A novel N, N, N-tridentate ligand known as 2-(2-pyridylmethylamino)ethylbenzimidazole (pymaeb) was designed and synthesized. This ligand in combination with disodium pyridine-2, 6-dicarboxylate (pydic) reacted with $RuCl_3$ to afford a novel complex Ru[2-(2-pyridymethylimino)ethylbenzimidazole]pyridinedicarboxylate [Ru(pymieb)(pydic)] which was characterized by NMR, IR, HR-MS and single crystal X-ray diffraction. Crystal structure analysis revealed that the complex has a distorted octahedral geometry. The complex showed excellent activity for the oxidation of various alcohols with TBHP as oxidation under mild and solvent-free conditions.

Keywords: N, N, N-tridentate ligand; ruthenium(II) complex; *tert*-butyl hydroperoxide; oxidation; alcohols

1. Introduction

The oxidation of alcohols to the corresponding carbonyl compounds plays an important role in both laboratory and synthetic industrial applications [1-6]. In traditional oxidation processes, large amounts of metal oxidants and toxic and volatile organic solvents were extensively used, which would generate large amounts of byproducts and cause pollution to the environment [7-11]. It would be of great economical and ecological importance to develop benign and clean processes by using molecular oxygen, hydrogen peroxide and *tert*-butyl hydrogen peroxide (TBHP) as oxidants. With this view, a variety of transition metal based catalysts [12-26], especially ruthenium compounds have been intensively studied due to their sufficiently selective and tolerant to many other functional groups [17-26]. For example, Ishii and his co-workers employed a phosphine ruthenium $Ru(PPh_3)_3Cl_2$ in combination with hydroquinone as a catalyst system in the aerobic oxidation of primary alcohols to their corresponding aldehydes in $PhCF_3$ [17]. They also applied $Ru(PPh_3)_3Cl_2$ supported on active carbon to the oxidative cleavage of *vic*-diols by dioxygen to the corresponding aldehydes [18]. Some ruthenium-nitrogen ligand complexes were also developed in the oxidation of alcohols. Katsuki successfully achieved the oxidation of primary alcohols to aldehydes in the presence of secondary alcohols under aerobic conditions by using a (nitrosyl)Ru(salen) complex as catalyst [19-21]. Ji developed a protocol for the selective aerobic oxidation of various alcohols to carbonyl compounds catalyzed by ruthenium(III) meso-tetraphenylporphyrin chloride in the presence of isobutyraldehyde [22]. In this case the dosage of

the catalyst was reduced dramatically. Recently, Ji and his co-workers synthesized a ruthenium-nitrogen ligand complex, ruthenium-bis(benzimidazole)pyridinedicarboxylate [27]. By applying this complex as catalyst, primary and secondary alcohols were oxidized to aldehydes and ketones in good yield and excellent selectivity under mild conditions with aqueous hydrogen peroxide as oxidant. The tridentate nitrogen liand bis(benzimidazole)pyridine is of very importance in determining the catalysis of the complex. This work indicates that it is possible to obtain complexes with various catalytic performances by designing and synthesizing novel ligands in homogeneous catalysis.

Our interest has been aroused by ruthenium-catalyzed oxidation reactions with its wide range of applicability and broad variation of ligand types in homogeneous catalysis, especially in the oxidation of alcohols. In this regard, we focus on designing and synthesizing a novel N,N,N-tridentate ligand with both benzimidazole and pyridine moieties, known as 2-(2-pyridylmethylamino)ethylbenzimidazole (pymaeb). This ligand in combination with disodium pyridine-2,6-dicarboxylate (pydic) reacted with $RuCl_3$ to afford a complex Ru[2-(2-pyridylmethylimino)ethylbenzimidazole]pyridinedicarboxylate [Ru(pymieb)(pydic)]. The complex showed excellent performances in the oxidation of alcohols with TBHP as oxidant under mild and solvent-free conditions without any additives. Herein, we report the synthesis, characterization and catalysis of the novel complex.

2. Experimental

2.1 Reagent and apparatus

2, 6-Pyridinedicarboxylic acid, β-alanine, 1,2-diaminobenzene, 2-pyridinecarbaldehyde and di-tert-butyl dicarbonate were purchased from Tianjin Keruisi Fine Chemical Co., LTD. Alcohols, ruthenium chloride and *t*-butyl hydroperoxide (TBHP) (70%) were obtained from Alfa Aesar China (Tianjin) Co., Ltd. Disodium pyridine-2, 6-dicarboxylate (pydic) was prepared by treatment of 2,6-pyridinedicarboxylic acid with sodium hydroxide. Other reagents were commercially available and used without further purification.

^{1}H NMR and ^{13}C NMR spectra were recorded with TMS as internal standard on a Brucker AC-P 400 type nuclear magnetic resonance spectrometer. Infrared spectra were obtained from a Bruker Vector 22 type instrument in the range 4000~400 cm^{-1} using a KBr pellet. Mass spectra were recorded on a VG ZAB-HS high-resolution spectrometer.

2.2 Synthesis of 2-(2-pyridylmethylamino)ethylbenzimidazole (pymaeb)

(1) Synthesis of 3-(*t*-butyloxycarbonyl)aminopropionic acid (**1**)

To β-alanine (4.45g, 0.050mol) in a 250 ml flask was added slowly 1N aqueous solution of NaOH (50 ml) at 0~5℃. Then a solution of di-tert-butyl dicarbonate (11.78g, 0.055mol) in 20ml of dioxane was added. The resulting mixture was slowly warmed to room temperature and

maintained overnight under stirring. After reaction the mixture was evaporated under vacuum and the residue was treated with 6N HCl to adjust the pH to 2~3. The mixture was extracted with ethyl acetate, washed with water, dried over Na_2SO_4 and concentrated under vacuum successively. The residue was recrystallized from ethyl acetate/n-hexane to give a white solid (8.35g, yield 88%). M.p. 76.1~77.6℃. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 1.45 (s, 9H, -$(CH_3)_3$), 2.59 (s, 2H, CH_2), 3.40 (s, 2H,CH_2),5.06 (s,1H,NH); IR(KBr, cm^{-1}) υ: 3440, 2981, 2701, 2632, 2574, 1705, 1515.

(2) Synthesis of N-(2-amino)phenyl-3-(*t*-butyloxycarbonyl)amino propionamide (**2**)

To a solution of **1** (7.56g, 0.04mol) in anhydrous dichloromethane (80ml) were added 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl) (11.50g, 0.06mol) and 1,2-diaminobenzene (6.48g, 0.06mol) at 0~5℃. The reaction mixture was stirred at room temperature for 7.5 h. Then the solution was quenched with saturated sodium carbonate solution, and extracted with ethyl acetate. The combined extracts were dried over Na_2SO_4 and evaporated under vacuum. The residue was recrystallized from ethyl acetate to afford a white solid (5.76g, yield 52%). M.p. 139.4~140.1℃. ^{1}H NMR(400 MHz, $CDCl_3$, TMS), δ(ppm): 1.43 (s, 9H, - $(CH_3)_3$), 2.61 (t, J=5.6Hz, 2H, CH_2), 3.46~3.50 (m, 2H, CH_2), 4.13 (s, 2H, NH_2), 5.25 (s, 1H, Ph-NH), 6.75~6.83(m, 2H, PhH), 7.04~7.08 (m, 1H, PhH), 7.21~7.26 (m, 1H, PhH), 7.74 (s, 1H, BocNH); IR (KBr, cm^{-1}) υ: 3458, 3372, 3328, 2978, 1689, 1648, 1533, 875, 745.

(3) Synthesis of 2-(2-(*t*-butyloxycarbonyl)amino)ethyl-1H-benzimidazole (**3**)

Intermediate **2** (8.38g, 0.03mol) was dissolved in glacial AcOH (35ml). The resulting solution was heated at 65℃ for 2.5 h. After reaction the mixture was evaporated under vacuum, and the residue was treated with saturated sodium carbonate solution. The resulting mixture was extracted with ethyl acetate and the combined extracts were dried over Na_2SO_4. The filtrate was evaporated to give a white solid (7.56g, yield 96%). M.p. 176.3~177.3℃. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 1.41 (s, 9H, -$(CH_3)_3$), 3.18 (t, J=6.0Hz, 2H, CH_2), 3.68~3.72(m, 2H, CH_2), 5.37 (s, 1H, Ph-NH), 7.21~7.27 (m, 2H, PhH), 7.55~7.57 (m, 2H, PhH); IR(KBr, cm^{-1}) υ:3427, 2972, 1719, 1502, 1417, 869, 752.

(4) Preparation of 2-aminoethylbenzimidazole·2TFA(**4**)

Intermediate **3** (7.84g,0.03mol) was dissolved in TFA (40 ml), and the resulting solution was stirred at room temperature for 0.5 h. Ether-petroleum mixture (1:1, v/v) was added to the solution until a white solid product precipitated. The mixture was filtered to give the product (11.56g, yield 99%). M.p. 157.6~158.5. ^{1}H NMR (400 MHz, D_2O, TMS), δ(ppm): 3.52~3.57 (m, 4H, $(CH_2)_2$), 7.50~7.53 (m, 2H, PhH), 7.68~7.71 (m, 2H, PhH); IR (KBr, cm^{-1}) υ: 1680, 1468, 1428, 841, 755.

(5) Synthesis of ligand pymaeb

To a solution of 4 (11.29g, 0.03mol) in anhydrous methanol (50ml) was added triethylamine (16ml, 0.11mol) under nitrogen atmosphere. 2-Pyridinecarbaldehyde (2.80ml, 0.03mol) was added dropwise. The resulting solution was stirred at 10□ for 15min, then $NaBH_4$ (2.18g, 0.06mol) was

added in portions carefully. After 3 h the reaction was quenched with water, and the mixture was evaporated under vacuum to give a residue. The resulting residue was dissolved in ethyl acetate, washed with water, dried over Na_2SO_4. The filtrate was evaporated under vacuum to remove the solvent. The residue was recrystallized from ethyl acetate to give a white solid product pymaeb (4.72g, yield 65%). M.p. 142.1~143□. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 3.15 (s, 4H, CH_2CH_2), 4.08 (s, 2H, CH_2), 7.19~7.28 (m, 4H, PhH), 7.56~7.58 (m, 2H, PyH), 7.67 (t, J= 4.0Hz, 1H, PyH), 8.68 (d, J=8Hz, 1H, PyH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ(ppm): 28.8, 46.4 (NH-CH_2-CH_2), 54.0 (NH-CH_2-Py), 114.7 (benzene ring), 121.8 (pyridine ring), 122.4 (benzene ring), 122.6 (pyridine ring), 136.8 (pyridine ring), 138.4 (benzene ring), 149.2 (pyridine ring), 154.7 (N=C-NH), 158.8 (pyridine ring); IR (KBr, cm^{-1}) υ: 3272, 3052, 2839, 1590, 1542, 1432, 1272, 750. HRMS(ESI+): m/z calcd. for $C_{15}H_{16}N_4 + H^+$: 253.1453; found: 253.1450.

2.3 Synthesis of complex

To a solution of pymaeb (0.76g, 3.0mmol) and $RuCl_3$ (0.62g, 3.0mmol) in methanol (23ml), pydic (0.63g, 3.0mmol) in MeOH/H_2O (1:1, 30 ml) was added in air. The resulting reaction mixture was heated at 65□ for 3h. After reaction the reaction mixture was cooled to room temperature. The dark violet precipitate was collected by filtration to give one part of product (0.56g). The filtrate was evaporated, washed with hot MeOH/H_2O (1:1, 20 ml), cooled to room temperature. Another part of the dark violet precipitate was formed, and collected by filtration (0.15g). Finally the product (0.71g, yield 46%) was received. ^{1}H NMR (400 MHz, CD_3OD, TMS), δ(ppm): 3.58 (t, J=8.0Hz, 2H, CH_2), 5.10 (t, J=8Hz, 2H, CH_2), 6.34 (d, J=8.4Hz, 1H, PhH), 6.89~6.93 (m, 1H, PhH), 7.16~7.19 (m, 2H, PhH), 7.28~7.31 (m, 1H, PyH), 7.47 (d, J=8.0Hz, 1H, PyH), 7.71~7.74 (m, 1H, PyH), 8.18 (d, J=8.0Hz, 1H, PyH), 8.32~8.41 (m, 3H, PyH), 9.56 (s, 1H, N=CH); IR (KBr, cm-1) υ: 3419, 2910, 1615, 1561, 1522, 1514, 1462, 752, 690; HRMS(ESI +): m/z calcd. for $C_{22}H_{17}O_4N_5Ru + H^+$: 518.0402; found: 518.0405. UV/Vis (MeOH) λ_{max}=378 nm, 526nm.

2.4 Catalytic oxidation of alcohols

In a typical process, into a 5 ml two-necked, round-bottom flask equipped with a magnetic stirrer and a thermometer were added the ruthenium complex [Ru(pymieb)(pydic)] (0.002mmol) and the substrate alcohol (2mmol) successively. The mixture was heated to 40 ℃ under stirring. Then *t*-butyl hydroperoxide (TBHP) was added dropwise to the mixture and the temperature was kept at 40 ℃ until completion of the reaction. The reaction samples were analyzed on a Shandong Lunan Ruihong Gas Chromatograph (SP-6800A) equipped with a FID detector and a SE 30 column (30 m×0.5 mm). The conditions used in gas chromatography were temperature of the detector 280□, column temperature 130–220□ (varying with alcohols), pressure of the carrier gas 0.05–0.07 MPa (varying with alcohols).

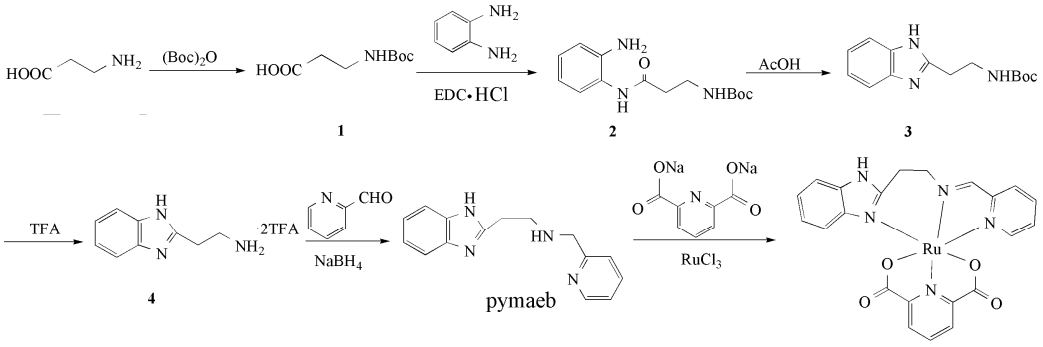
2.5 X-ray structure determination

Crystal suitable for X-ray crystallography was obtained by slow diffusion of THF to a solution of the complex in DMF at room temperature. The single crystal X-ray diffraction data collection for the complex was performed with a Rigaku Saturn70 CCD diffractometer, equipped with graphite monochromatized Mo radiation with a radiation wavelength of 0.071073 nm. All the calculation was accomplished by using program of SHELXS-97 and SHELXL-97.

3. Results and discussion

3.1 Synthesis of complex

The synthesis route of the ruthenium complex is shown in Scheme 1. First, the ligand pymaeb was synthesized in five steps. In the first step the Boc protected β-alanine, 3-(*t*-butyloxycarbonyl)aminopropionic acid **(1)**, was smoothly synthesized from β-alanine and di-tert-butyl dicarbonate. In the next step the carboxy group of **1** condensed with one amino group of 1,2-diaminobenzene in the presence 1-(3-dimethyl aminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl) as condensing agent to afford the amide (**2**) in moderate yield. This amide underwent a ring closure upon intra-molecular condensation of the carbonyl group with the *ortho* amino group to form the benzimidazole ring readily to give intermediate **3**. The protecting group BOC was easily removed by resolving **3** in TFA, and the released amino group reacted with TFA in situ to form a salt. The obtained salt proceeded reductive amination with 2-pyridinealdehyde using $NaBH_4$ as reducing agent and triethylamine as acid scavenger to give the ligand pymaeb. The reaction of $RuCl_3$ with pymaeb and pydic in 1:1:1 molar ratio in refluxing MeOH/H_2O (1:1) afforded the complex as shown in Scheme 1. The formation of the complex involves the dehydrogenation of pmaeb to 2-(2-pyridymethylimine)ethylbenzimidazole (pymieb), while the Ru(III) is reduced to Ru(II).



Scheme 1. Synthesis route for the ruthenium complex

3.2 Spectral characterization

The structure of pymaeb and the complex were characterized by ^{1}H NMR, FT-IR and HR-MS thoroughly. In the ^{1}H NMR spectrum of pmaeb (Fig. S1) resonance at 3.98 ppm (single peak) is

assigned to the 2 protons of the methylene attached to the pyridyl ring; the resonances at 3.57~3.60 and 5.09~5.11 ppm are assigned to the 4 protons of the ethylene group. The ^{13}C NMR of the pmaeb as shown in Fig. S2 is in agreement with that of the expected structure. In the ^{1}H NMR spectrum of the complex (Fig. S3) the resonance corresponding to the 2 protons of the methylene attached to the pyridyl ring in pymaeb is disappeared; instead, a resonance at 9.56 ppm (s, 1H) which can be assigned to that of the 1 proton of imino group formed from the dehydrogenation of the aminomethyl moiety attached to the pyridyl ring in pymaeb is observed.

In the FT-IR spectrum of pymaeb two bands respectively exhibited at 1590 and 1542 cm^{-1} are assigned to the C=N stretching vibrations of pyridine and benzimidazole moieties [28]. These bands shift to 1561 and 1514 cm^{-1} in the ruthenium complex, indicating the coordination of pyridine and benzimidazole nitrogens to the ruthenium (Fig. S29). In addition the band around 3272 cm^{-1} due to the N-H vibration of the secondary amino group in pymaeb disappears in the ruthenium complex, indicating the secondary amine is converted to other group in the complex [29].

The UV–Vis absorption spectrum of the complex was investigated in the 200–800 nm range in MeOH as shown in Fig. S30. The spectrum of the complex shows bands in the region 230-530nm. The ruthenium complex is diamagnetic, indicating the presence of ruthenium in the +2 oxidation state. The ground state of ruthenium(II) in an octahedral environment is $^{1}A_{1g}$, arising from the t_{2g}^{6} configuration, and the excited states corresponding to the $t_{2g}^{5}e_{g}^{1}$ configuration are $^{3}T_{1g}$, $^{3}T_{2g}$, $^{1}T_{1g}$ and $^{1}T_{2g}$. Hence, four bands corresponding to the transitions $^{1}A_{1g} \rightarrow {}^{3}T_{1g}$, $^{1}A_{1g} \rightarrow {}^{3}T_{2g}$, $^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ and $^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ are possible in order of the increasing energy [30]. The bands appearing in the region 230-280 nm are assigned to intraligand transitions [24, 31]. These bands are designated as π-π^* and n-π^* transitions for the electrons localized on the aromatic system. The band due to charge transfer transitions arising from the metal t_{2g} level to the unfilled π^* molecular orbital of the ligand appears around 378nm. The electronic spectral band at 526nm is assigned to d–d transition. The pattern of the electronic spectrum indicates the presence of an octahedral geometry around ruthenium(II) ion [32,33].

3.3 X-ray crystallography of ruthenium complex

The crystal structure of the complex was determined by means of X-ray structure determination. The molecular structure of the complex is illustrated in Fig. 1. Details of the X-ray experiment, crystal parameters, data collections and refinements are summarized in Table 1, and the selected bond lengths and angles are listed in Table 2.

Crystal structure analysis revealed that the complex belongs to a monoclinic system with space group P2(1)/c. As shown in Fig.1, the crystal structure of the complex contains one water molecule. The central ruthenium atom is coordinated by pymieb from the dehydrogenation of pymaeb in the formation of the complex, as well as pybic. The pymieb coordinates to ruthenium ion via the pyridine nitrogen (N4), benzimidazole nitrogen (N1) and imine nitrogen (N3). The

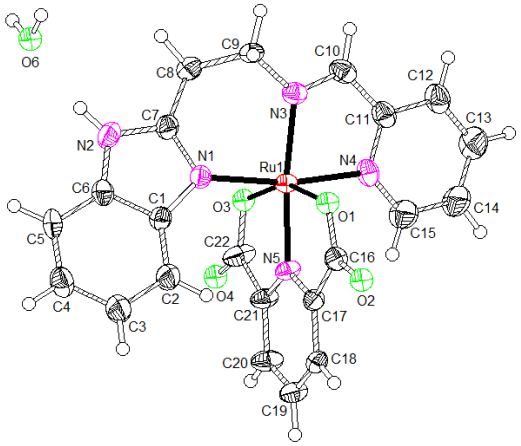


Fig.1. Molecular structure of ruthenium complex

pydic binds the metal center at the pyridine nitrogen (N5) and carboxylate oxygen (O1, O3). The pymieb coordinates to Ru on one plane as a N,N,N-tridentate ligand and the pydic acts as a dianionic O,N,O-tridentate ligand on another plane, in which they are nearly perpendicular to each other. The geometry around Ru1 can be described as a distorted octahedral geometry, in which the four nitrogen atoms occupy the four equatorial positions, while the two oxygen atoms are in the axial with a trans-position. The selected bond lengths and angles for the complex are shown in Table 2. The distances of Ru(1)-N(1), Ru(1)-N(3) and Ru(1)-N(4) are 2.101(4), 2.018(4) and2.056(4) Å, respectively, which indicates that imino group coordinates to Ru(II) more strongly than benzimidazolyl and pyridyl groups in pymieb. The distance of Ru(1)-N(5) is 1.967(4) Å shorter than the ones of Ru(1)-N(1), Ru(1)-N(3) and Ru(1)-N(4). This difference arises from higher steric hindrance of pymieb than pybic.

Table 1 Crystallographic data for the complex

Empirical formula	$C_{22}H_{17}N_5O_4Ru \cdot H_2O$	Size / mm	0.22 × 0.18× 0.12
Formula weight	534.49	F(000)	1080
Temperature /K	113(2)	Absorption coefficient/ mm^{-1}	0.674
Wavelength/ Å	0.71073	θ range for data collection / (°)	2.17 to 27.95
Crystal system	Monoclinic	Limiting indices	-12 ⩽h⩽11, -32⩽k⩽32, -14 ⩽l⩽14
space group	P2(1)/c	Reflections collected	21979
a / Å	9.7261(19)	unique	5830 [R_{int} = 0.0435]

b / Å	25.145(5)	Completeness to theta = 25.02	98.2 %
c / Å	10.903(2)	Absorption correction	Semi-empirical from equivalents
α/ (°)	90	Max. and min. transmission	0.9235 and 0.8658
β/ (°)	112.07(3)	Data / restraints / parameters	5830 / 0 / 306
γ/ (°)	90	Goodness-of-fit on F^2	1.029
V / Å^3	2471.2(9)	Final R indices [$I>2\sigma(I)$]	R_1 = 0.0740, wR_2 = 0.1876
Z	4	R indices (all data)	R_1 = 0.0802, wR_2 = 0.1932
D_c / (mg·m^{-3})	1.437	Largest diff. peak and hole/(e·Å^{-3})	5.959 and -1.518

Table 2 Selected bond lengths (Å) and angles (°) for the complex

Bond	Ru(1)-N(1)	2.101(4)	Ru(1)-N(4)	2.056(4)	Ru(1)-O(1)	2.109(3)
	Ru(1)-N(3)	2.018(4)	Ru(1)-N(5)	1.967(4)	Ru(1)-O(3)	2.121(4)
Angle	N(1)-Ru(1)-N(3)	91.08(17)	N(3)-Ru(1)-N(4)	78.74(17)	N(4)-Ru(1)-O(1)	91.63(16)
	N(1)-Ru(1)-N(4)	168.98(16)	N(3)-Ru(1)-N(5)	173.44(17)	N(4)-Ru(1)-O(3)	91.91(18)
	N(1)-Ru(1)-N(5)	95.35(16)	N(3)-Ru(1)-O(1)	99.94(14)	N(5)-Ru(1)-O(1)	78.35(14)
	N(1)-Ru(1)-O(1)	94.31(14)	N(3)-Ru(1)-O(3)	103.14(15)	N(5)-Ru(1)-O(3)	78.61(14)
	N(1)-Ru(1)-O(3)	86.26(16)	N(4)-Ru(1)-N(5)	94.94(17)	O(1)-Ru(1)-O(3)	156.90(14)

3.4 Catalytic oxidation of alcohols

Table 3 The oxidation of 1-phenylethanol catalyzed by the ruthenium complex with different oxidants

Entry	Oxidant [a]	Solvent	Time（h）	Conversion (%)[b]	Selectivity (%)[b]
1	O_2	CH_3CN	1.0	1.5	>99
2	30% H_2O_2	CH_3CN	1.0	11.2	>99
3	70% TBHP	CH_3CN	1.0	48.6	>99

4	70% TBHP	CH_3CN	10.0	76.9	>99
5	70% TBHP	CH_3OH	5.0	56.1	>99
6	70% TBHP	—	2.5	99.9	>99

Reaction condition: 1-phenylethanol (2 mmol), catalyst (0.1 mol%), oxidant (10 mmol), 40℃, solvent (2 ml).
[a] O_2 1 atm; [b] Determined by GC.

The complex was employed as a catalyst for the oxidation of various alcohols to the corresponding carbonyl compounds with TBHP as oxidant. Initially, different oxidants including O_2, H_2O_2 and TBHP were examined in the oxidation of 1-phenylethanol as a model substrate with acetonitrile as solvent. As shown in Table 3 almost no reaction took place in the case of atmospheric oxygen as oxidant (Table 3, entry 1). Unexpectedly, very low conversion was received when 30% aqueous H_2O_2 was used as oxidant, which is very different from the same reaction catalyzed by a similar complex Ru(bbp)(pybic) (Table 3, entry 2)[27]. TBHP showed good performance in the reaction. The conversion of 1-phenylethanol reached up to 48.6% in 1 h, and increased with reaction time (Table 3, entries 3 and 4).

The reaction was also run in methanol and solvent-free conditions, respectively. It can be seen that the reaction proceeded slowly in methanol, and only moderate conversions of 1-phenylethanol were obtained in more than 5 h (Table 3, entries 4 and 5). However, 1-phenylethanol was quantitatively converted to acetophenone in 2.5 under solvent-free conditions. It is advantageous to perform the reaction under solvent-free conditions due to no requirement of solvent separation.

Table 4 Necessity of the ruthenium complex in the oxidation of 1-phenylethanol with TBHP as oxidant

Entry	Catalyst	Amount (mol%)	Time (h)	Conversion (%)[a]	Selectivity (%)[a]
1	Ru(pymieb)(pydic)	0	3	28.6	>99
2	Ru(pymieb)(pydic)	0.10	2.5	99.8	>99
3	$RuCl_3$	0.10	3	43.0	>99
4	$RuCl_3$/pymaeb	0.10/0.10	8	64.4	>99
5[b]	$[Et_3NH]_2[Ru(dipic)Cl_3]$	0.10	8	71.6	>99

Reaction conditions: 1-phenylethanol 2 mmol, TBHP 6 mmol, catalyst 0.002mmol (0.1 mol%), reaction temperature 40℃. [a] Conversions and selectivity were determined by GC (area normalization method); [b] Complex $[Et_3NH]_2[Ru(dipic)Cl_3]$ is obtained from direct coordination of $RuCl_3$ with 2,6-pyridinedicarboxylic acid in the presence of triethylamine [34] .

Control experiments were performed with 1-phenylethanol as substrate to evaluate the necessity of the complex in the oxidation of alcohols with TBHP as oxidant. As shown in Table 4, the use of complex Ru(pymieb)(pydic) is essential. Only 28.6 % of 1-phenylethanol was converted to

acetophenone in 3 h when no Ru(pymieb)(pydic) was added (Table 4, entry 1). However, the conversion of 1-phenylethanol reached up to 99.8% in 2.5 h if only 0.10 % mole of Ru(pymieb)(pydic) was introduced (Table 4, entry 2). When $RuCl_3$ instead of Ru(pymieb)(pydic) was used as catalyst, the conversion of 1-phenylethanol was 43.0 % in 3 h (Table 4, entry 3). If both $RuCl_3$ and pymaeb were introduced, the reaction was improved and the conversion of 1-phenylethanol reached 64.4 % in 8 h (Table 4, entry 4). Complex $[Et_3NH]_2[Ru(dipic)Cl_3]$ pre-prepared from direct coordination of $RuCl_3$ with 2,6-pyridinedicarboxylic acid in the presence of triethylamine also had poor performance compared to Ru(pymieb)(pydic). In the case of this complex as catalyst the conversion of 1-phenylethanol was 71.6 % in 8 h (Table 4, entry 5).

The effect of reaction parameters was examined by running the reaction in solvent-free conditions, and the results are listed in Table 5. As can be seen from Table 5, the reaction rate increased with increasing the molar ratio of TBHP to 1-phenylethanol, and the reaction completed in the same time if the molar ratio was higher than 3:1 (Table 5, entries 1-4). Increasing the complex loading from 0.050 mol% to 0.20 mol% led to fast reaction, the reaction time required to finish the reaction decreased from 5.0 h to 1.5 h (Table 5, entries 6 and 7). Meanwhile, increasing the reaction temperature can accelerate the reaction (Table 5, entries 2, 8 and 9). From the results we found the optimal amounts of TBHP and complex to be 3 equivalents and 0.1 mol%, respectively, and the suitable reaction temperature to be 40℃.

Table 5 Optimization of reaction conditions under solvent free conditions [a]

Entry	Substrate：TBHP[b]	Complex（mol%）	T (℃)	Time (h)	Conv.[c, d] (%)
1	1：5	0.10	40	2.5	99.9
2	1：3	0.10	40	2.5	100
3	1：2	0.10	40	5.0	99.1
4	1：1.1	0.10	40	7.0	78.8
5	1：3	0.00	40	3.0	28.6
6	1：3	0.050	40	5.0	99.9
7	1：3	0.20	40	1.5	99.4
8	1：3	0.10	20	9.0	99.7
9	1：3	0.10	60	1.5	99.9

[a] 1-Phenylethanol (2 mmol); [b] Molar ratio; [c] Determined by GC; [d] Selectivity >99%

In order to evaluate the versatility of this novel catalytic system, the oxidation of various alcohols to the corresponding carbonyl compounds was explored under the optimized reaction conditions, and the results are shown in Table 6. As shown in Table 6, most of secondary benzylic

alcohols, including those bearing both electron-withdrawing and electron-donating groups *para* or *meta* to hydroxyalkyl moiety, were selectively converted to their corresponding aromatic ketones in excellent yields under the optimal reaction conditions (Table 6, entries 1-6, 10-14). These alcohols are generally difficult to be oxidized by molecular oxygen catalyzed by copper/TEMPO based catalysts [35-38]. However, the time required to finish the reaction was different especially in the case of 4-fluoro-α-phenylethanol as a substrate (Table 6, entries 1-6). These results demonstrated that electronic effects seem to have some effects on the reaction of substrate with a substituent *para* to the -hydroxymethyl. The position of the substituent on the benzene ring has certain effects on the reactivity of benzylic alcohols, too. The substrate with an *o*-substituent showed poor reactivity compared to that with an *m*- or *p*-substituent due to the steric hindrance (Table 6, entries 7, 8). For instance, only 49.5% conversion was obtained in 12.5 h in the case of 1-(2-chlorophenyl)ethanol as a substrate (Table 6, entry 8). Overall, the reaction rate was determined by the combination of the electronic and steric effects. The complex showed moderate activity in the oxidation of secondary aliphatic alcohols which are poor substrates in most of the transition-metal catalyst systems (Table 6, entries 15, 16) [35-38]. 2-Isopropyl-5-methylcyclohexanol gave very low conversion due to the big steric hindrance in the structure (Table 6, entry 17).

The protocol was also applied to the oxidation of primary benzylic alcohols. Meanwhile, we want to see whether it was possible to obtain selectivity towards either the aldehyde or the carboxylic acid. Unfortunately, the selectivity was not controlled, the main products were the carboxylic acids (Table 6, entries 18-22). However, the primary heterocyclic alcohols including 2-thioyl methanol, 2-pyridyl methanol and 5-hydroxymethylfurfural were converted to the corresponding aldehydes in moderate conversion, and no deep oxidation products were observed (Table 6, entries 23-25). A drawback of this protocol is that it does not work well with aliphatic alcohols similar to the results catalyzed by other Ru-based catalytic system [39].

3.5 Mechanism aspect

A ruthenium (III) oxo complex or ruthenium(III) species was observed in several similar ruthenium complex-catalyzed oxidation systems [27,40,41]. In addition, a close-open equilibrium of an axial Ru–O bond of Ru(pyboxazine)(pydic) in solution was also detected by Beller [41]. For our complex Ru(pymieb)(pydic), the bond distance of Ru-O is longer than that of Ru-N (Table 2). When DMSO and THF were diffused into the complex solution in DMF, a carboxyl group dissociated from the central ruthenium ion by replacement of one DMSO molecule to form a novel complex Ru(pymieb)(pydic)(DMSO). The detailed crystal structure of the formed complex can be found in Supplementary information (Fig. S31). Based on these results in combination with our experimental result that the oxidation reaction rate was related with the steric hindrance of the substrate, and by reference of a mechanism proposed for a manganese(III) complex-

catalyzed oxidation of alcohols with TBHP as oxidant [42], we propose a possible mechanism for the alcohol oxidation catalyzed by this ruthenium complex as shown in Scheme 2.

Table 6 Oxidation of various alcohols by TBHP in the presence of ruthenium complex

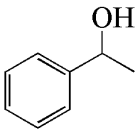
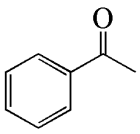
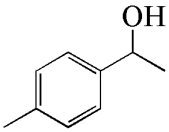
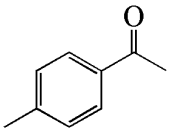
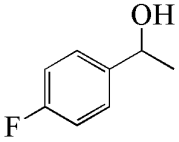
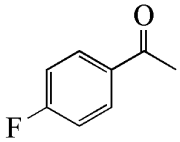
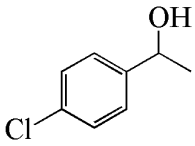
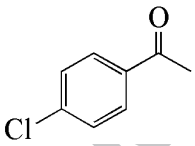
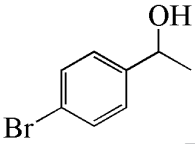
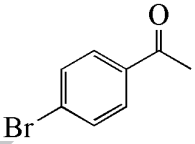
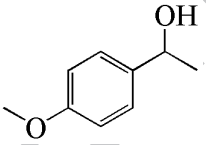
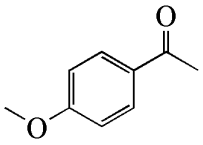
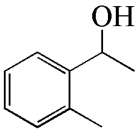
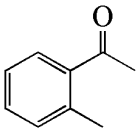
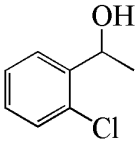
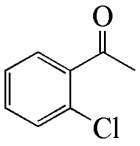
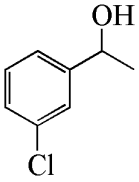
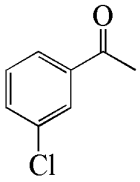
Entry	Substrate	Product	Time (h)	Conversion[a] (%)	Selectivity[a] (%)
1			2.5	100(95)	>99
2			2.5	100	>99
3			6.0	99.1	>99
4			3.0	99.8(96)	>99
5			3.0	100	>99
6			3.0	99.7(95)	>99
7			12.0	88.9	>99
8			12.5	49.5	>99
9			4.0	99.9	>99

Table 6 (continued)Oxidation of various alcohols by TBHP in the presence of ruthenium complex

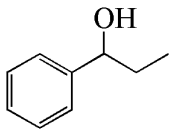
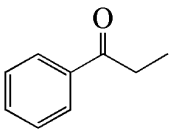
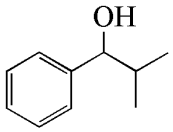
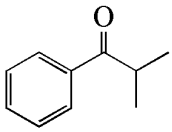
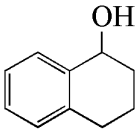
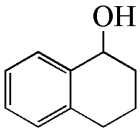
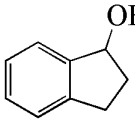
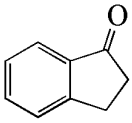
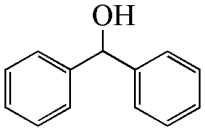
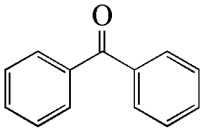
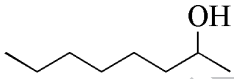
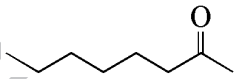
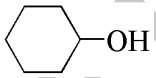
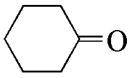
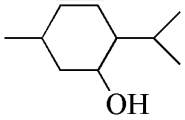
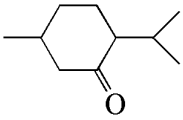
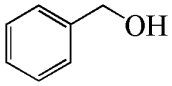
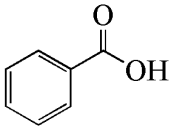
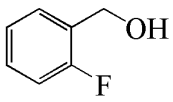
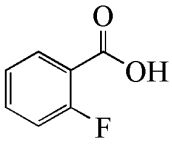
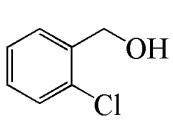
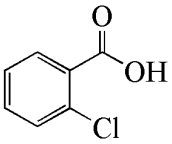
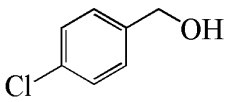
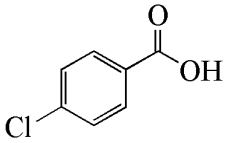
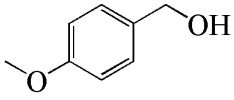
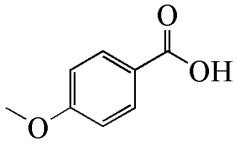
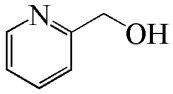
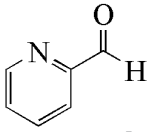
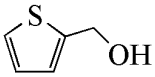
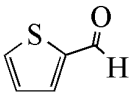
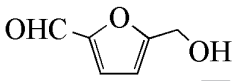
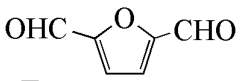
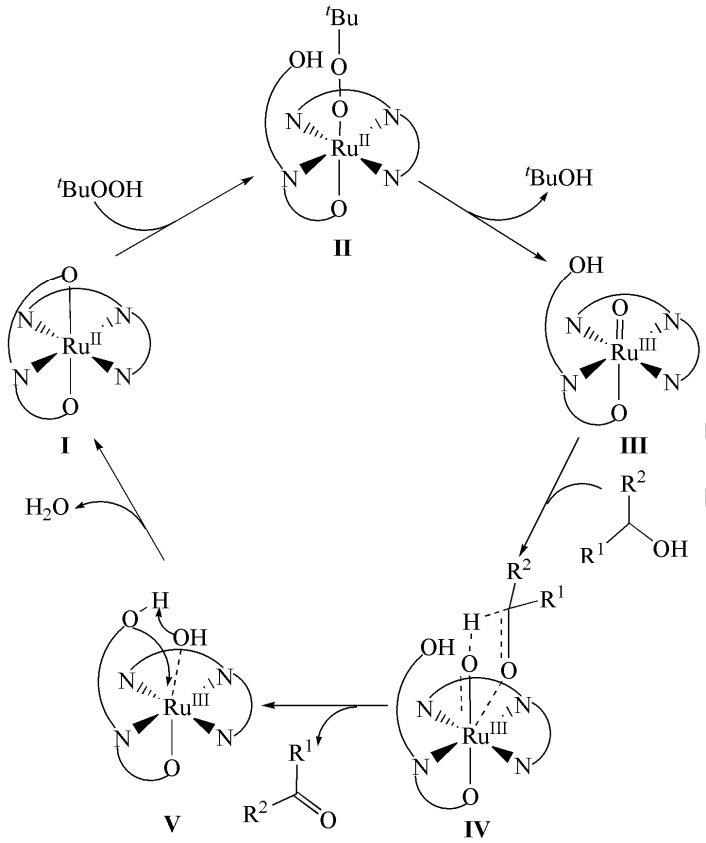
Entry	Substrate	Product	Time (h)	Conversion [a] (%)	Selectivity [a] (%)
10			4.0	100(95)	>99
11			8.0	97.2	>99
12			2.0	100	>99
13			1.0	99.7	>99
14			1.5	100(95)	>99
15			4.5	55.1	98.9
16			13.0	83.9	>99
17			5.0	27.0	>99
18			3.5	99.6	88.5
19			7.5	99.5	95.6

Table 6(continued)Oxidation of various alcohols by TBHP in the presence of ruthenium complex

Entry	Substrate	Product	Time (h)	Conversion[a] (%)	Selectivity[a] (%)
20			11.5	99.7	92.7
21			6.0	99.9	95.6
22			10.0	99.8	88.3
23			2.0	44.5	>99
24			3.5	78.4	>99
25			7.0	60.3	87.9

Reaction conditions: alcohol 2 mmol, TBHP 6 mmol, catalyst 0.002mmol (0.1 mol%), reaction temperature 40℃.
[a] Conversions and selectivity were determined by GC (area normalization method); data in parentheses were isolated yields; all products were determined by ^{1}H NMR.

In the oxidation process, the Ru(II) complex (**I**) readily interacts with TBHP to form a Ru(III)–OO^{t}Bu species **II** through opening an axial Ru–O bond. Then species **II** forms the ruthenium (III) oxo complex (**III**) through the heterolytic cleavage of O–O bond, and releases *t*-butyl alcohol. **III** as a strong oxidant converts alcohol to the corresponding ketone or aldehyde through a transition state (**III**), and simultaneously gives species **V**. The intermediate **V**, on the loss of the water molecules through the re-coordination of the carboxy of pybic, eventually gives the regenerated Ru(II) complex **I**.



Scheme 2 Possible catalytic cycle for the complex-catalyzed oxidation of alcohols with TBHP as oxidant

4. Conclusion

A N,N,N-tridentate ligand known as 2-(2-pyridymethylamino)ethylbenzimidazole (pymaeb) was synthesized. This ligand in combination with disodium pyridine-2,6-dicarboxylate (pybic) reacted with $RuCl_3$ to afford a novel complex Ru(pymaeb)(pybic). During the reaction the liangd pymaeb was dehydrogenated to 2-(2-pyridymethylimino)ethylbenzimidazole (pymaeb) and Ru(III) was reduced to Ru(II). The Ru(II) complex was thoroughly characterized by NMR, IR, HR-MS and single crystal X-ray diffraction. Crystal structure analysis revealed that the complex has a distorted octahedral geometry. The ruthenium was employed as catalyst for the oxidation of various alcohols with TBHP as oxidant. Under the catalysis of this complex secondary benzylic alcohols and primary benzylic alcohols were quantitatively oxidized to their corresponding ketones and acids, respectively, under mild and solvent-free conditions. This complex also showed moderate activity in the oxidation of secondary aliphatic alcohols and primary heterocyclic alcohols to the corresponding ketones and aldehydes under the same conditions.

Appendix A. Supplementary data

CCDC <1405850> contains the supplementary crystallographic data for Ru(pymaeb)(pybic). CCDC <1417328> contains the supplementary crystallographic data for the complex Ru(pymieb)(pydic)(DMSO). These data can be obtained free of charge via

http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

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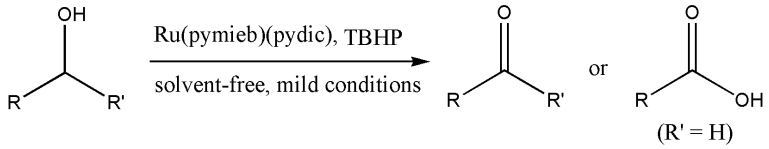
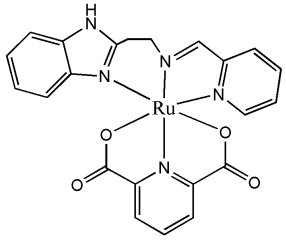
Graphical abstract synopsis

A novel Ru(II) complex Ru(pymieb)(pydic) was synthesized and characterized by NMR, FT-IR, HR-MS and single crystal X-ray diffraction. The complex showed excellent activity for the oxidation of various alcohols with TBHP as oxidant under mild and solvent-free conditions.

Graphical abstract pictogram





Ru(pymieb)(pydic)