

Oxidation of alcohols using iodosylbenzene as oxidant catalyzed by ruthenium complexes under mild reaction conditions

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Abstract

Aromatic and alkyl alcohols were oxidized to the corresponding aldehydes or ketones at room temperature with high conversion and selectivity to the desired products of 100% using iodosylbenzene as oxidant catalyzed by ruthenium complexes Phen-Ru-Phen, Phen-Ru-Bipy, Phen-Ru-Quin, Quin-Ru-Quin and Bipy-Ru-Quin (where Phen = 1,10-phenanthroline, Quin = 8-hydroxyquinoline, Bipy = 2,2'-bipyridine). The reaction conditions are mild, the ligands used in this oxidation system are commercially available and the procedure for the preparation of the complexes is very simple. © 2006 Elsevier B.V. All rights reserved.

Keywords: Alcohols; Catalytic oxidation; Ruthenium complexes; Iodosylbenzene

1. Introduction

The oxidation of alcohols to corresponding aldehydes or ketones is a fundamental reaction in organic synthesis since the resulting compounds are quite useful synthetic intermediates especially for the construction of carbon-skeletons [1,2]. Numerous oxidizing reagents are available to achieve this key transformation, e.g. chromium(VI)-based oxidants [3,4], activated dimethylsulfoxides [5,6] and hypervalent iodines [7,8]. Although these methods are useful in organic synthesis, each contains problems to be solved. In most instances, the reagents are used in stoichiometric amounts and are often toxic such as the chromium oxidants used in vast amounts in both the laboratory and industry. However, with the overgrowing environmental and economic concerns the development of benign catalytic processes for alcohol oxidation is becoming increasingly important.

Catalytic oxidation methods, which employ other metal-containing catalysts resulting in the avoiding of the use of such toxic reagents, developed quickly in recent decades. Metal-containing catalytic systems have been documented, such as Cu(I) [9–11], Ni(II) [12,13], Co(II) [14–16], Pd(II) [17–19] and manganese oxides [20,21]. Among these catalysts, ruthenium

complexes have been found to be active towards the oxidation of alcohols. However, the ligands and the methodology employed to prepare ruthenium complexes are generally very difficult [22–24]. Aimed at the simplification of the preparation of reactive ruthenium-based catalysts, we reported the preliminary result of our research on the oxidation of alcohols using ruthenium complexes as catalysts [25]. We have also reported the oxidation of alcohols catalyzed by a polymer-supported ruthenium complex [26]. Here we describe detailed results of the synthesis and the catalytic behavior of several ruthenium complexes obtained by the reaction of Ru(III) with 1,10-phenanthroline, 8-hydroxy-quinoline, and 2,2'-bipyridine, respectively. The ligands used in our system are commercially available and the complexes are prepared through a simple procedure. A series of benzylic and primary aliphatic alcohols were oxidized to the corresponding aldehydes or ketones catalyzed by these complexes.

2. Experimental

2.1. Reagents

1,10-Phenanthroline (Phen), 2,2'-bipyridine (Bipy) and 8-hydroxyquinoline (Quin) are all analytic pure reagents and were obtained from commercial sources. $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ ($x = 1-3$) is chemical pure reagent. All of the alcohols used in the reaction were obtained from ABCR GmbH & Co. KG. Other materials

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Table 1
The absorption signal of N–Ru and O–Ru peak of the complexes

Complexes	$\nu_{\text{N-Ru}}$ (cm^{-1})	$\nu_{\text{O-Ru}}$ (cm^{-1})
Phen-Ru-Phen	462	619
Phen-Ru-Bipy	463	620
Phen-Ru-Quin	462	618
Quin-Ru-Quin	486	609
Bipy-Ru-Quin	465	616

are analytic pure and were used as received without further treatment.

2.2. Preparation of different ruthenium-containing complexes

All of the complexes were prepared through simple procedures according to the literatures [27,28]. In anhydrous ethanol solutions containing identical amount of 1,10-phenanthroline (Phen), 2,2'-bipyridine (Bipy) and 8-hydroxyquinoline (Quin), the stoichiometric amount of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ was added, respectively, and some deposit was formed. The reaction mixture was stirred at 25 °C for 4 h, then cooled and filtered. The obtained sediment was then washed with anhydrous ethanol and dried under vacuum at 40 °C overnight, the different ruthenium complexes, abbreviated as Phen-Ru-Phen, Phen-Ru-Quin, Phen-Ru-Bipy, Quin-Ru-Quin and Quin-Ru-Bipy, were prepared.

2.3. Instrumentation

FT-IR spectra were recorded on a Nicolet NEXUS 670 FT-IR IR spectrometer using KBr disks. Metal content was measured on an American ICPV-5600 analytic instrument under the standard conditions. GC/MS analyses were carried out on a trace HP GC6890/MS5973 equipped with a 25 m \times 0.25 mm SE-54 column and a Shimadzu GC-16A gas chromatograph with a 3 m \times 3 mm OV-17 column. The content of C, N, and H was determined by GmbH Vario EL elemental analysis. The results are shown in Tables 1–3.

2.4. Characterization of the complexes

2.4.1. FT-IR

The special absorption peaks of N–Ru and O–Ru of the five complexes in their IR spectra were showed in the these spectrograms, and their wavenumbers are concluded in Table 1.

The IR spectra show that the absorption signal of N–Ru and O–Ru peaks were all appeared in the spectrograms. It can be

Table 2
The ICP determination results of the complexes

Complexes	Content of ruthenium (%)
Phen-Ru-Phen	8.0
Phen-Ru-Bipy	13.5
Phen-Ru-Quin	15.2
Quin-Ru-Quin	13.8
Bipy-Ru-Quin	11.9

Table 3
The results of elemental analysis of the five complexes

Complexes	C%	H%	N%
Phen-Ru-Phen	37.53	2.07	7.15
Phen-Ru-Bipy	32.91	1.80	6.56
Phen-Ru-Quin	33.11	2.06	7.52
Quin-Ru-Quin	32.54	2.13	5.73
Bipy-Ru-Quin	31.63	2.16	5.35

confirmed that the coordination bonds between Ru(III) and N and O atoms has been conformed through the reaction. For Phen-Ru-Phen and Phen-Ru-Bipy, Ru–O bond may come from the hydrolysis of Ru. But for other three complexes containing Quin in their structure, Ru–O bond may come both from the hydrolysis of Ru and Ru-ligand.

2.4.2. ICP

The content of ruthenium of the five complexes was also well determined with ICP method, and the results are shown in Table 2.

2.4.3. Elemental analysis

The five complexes were also characterized with elemental analysis. The content of C%, H%, and N% is shown in Table 3.

3. Results and discussions

3.1. Catalytic properties of the complexes for the oxidation of benzylalcohol

In order to investigate the catalytic properties of the complexes Phen-Ru-Phen, Phen-Ru-Bipy, Phen-Ru-Quin, Quin-Ru-Quin and Bipy-Ru-Quin, benzylalcohol was chosen as the substrate. The oxidation was carried out in a 10 mL glass reactor in CH_3CN at room temperature. We used a fixed amount of the benzylalcohol (0.1 mmol) and PhIO (2.5 equiv.), and changed the catalysts Phen-Ru-Phen, Phen-Ru-Quin, Phen-Ru-Bipy, Quin-Ru-Quin and Quin-Ru-Bipy. Benzylalcohol is oxidized in this oxidation system to give the corresponding benzaldehyde. The results are summarized in Table 4. We found that all of the complexes show high reactivity for the oxidation. The conversions are reached 100% in 1 h, 2 h, 4 h, 5 h, and 8 h by the utilization

Table 4
Catalytic oxidation of benzylalcohol by the ruthenium complexes

Catalysts	Time (h)	Conversion (%)	Selectivity (%)
Quin-Ru-Quin	1	100	100
Phen-Ru-Quin	2	100	100
Phen-Ru-Bipy	4	100	100
Quin-Ru-Bipy	5	100	100
Phen-Ru-Phen	8	100	100

Conditions: benzylalcohol 0.1 mmol, PhIO 0.25 mmol, catalyst 4 mg, CH_3CN 2 mL, 25 °C.

of the catalysts Quin-Ru-Quin, Phen-Ru-Quin, Phen-Ru-Bipy, Quin-Ru-Bipy and Phen-Ru-Phen, respectively.

It was showed in the table that all of the complexes were excellent catalysts for the oxidation of benzylalcohol in the system. However, among all of the complexes, the catalytic activity of the Quin-Ru-Quin complex is superior to those of the others. The results also suggest that complexes with 8-hydroxyquinoline as ligand generally possess higher reactivity.

3.2. Optimization of the oxidation conditions

In order to evaluate the catalytic activities of the complexes for the oxidation of other alcohols, the reaction condition was optimized according to the oxidation of benzylalcohol through the investigation of the influence factors of the oxidation, such as the temperature, the reaction time, the solvent, the amount of the catalyst used and the amount of PhIO consumed.

3.2.1. The reaction time

The influence of the reaction time on the catalytic conversion and selectivity was investigated by a series of oxidation reactions in which benzylalcohol was also chosen as test substrate for the oxidation with PhIO catalyzed by Quin-Ru-Quin. The reaction was done in CH₃CN at room temperature. The oxidation mixture was taken out with an identical interval at different reaction time, and was then determined through the GC (instrument: Shimadzu GC-16A chromatography) and GC/MS (GC/MS Trance 2000 Ins.) record immediately. The results are concluded in Table 5.

As shown in Table 5, the conversion of the substrate is 10%, 60%, 85%, 93%, 98% and 100% when the reaction conducted for 10 min, 20 min, 30 min, 40 min, 50 min and 1 h, respectively. The results suggest that the conversion increases with the reaction time and the selectivity to the product is kept 100% in all the reaction period ranged from 10 min to 1 h. Table 5 also shows that the reactions generally begin with relatively fast rates in the first 10–30 min in which the conversion increases from 10% to 85% but tend to slow down in 40–60 min in which the conversion is changed from 93% to 100%.

Within 1 h, benzylalcohol was transferred quantitatively to benzaldehyde. This suggests that the appropriate reaction time is 1 h. Concerning for the oxidation of other alcohols, since their structures differ largely, the reaction time of these alcohols will be adjusted accordingly.

Table 5
Catalytic oxidation of benzylalcohol in different reaction time by Quin-Ru-Quin

Entry	Time (min)	Conversion (%)	Selectivity (%)
1	10	10	100
2	20	60	100
3	30	85	100
4	40	93	100
5	50	98	100
6	60	100	100

Conditions: benzylalcohol 0.1 mmol, PhIO 0.25 mmol, catalyst 4 mg, CH₃CN 2 mL, 25 °C.

Table 6
Catalytic oxidation of benzylalcohol in different solvents with Quin-Ru-Quin

Entry	Solvent	Conversion (%)	Selectivity (%)
1	DCM	58	100
2	THF	31	100
3	Toluene	18	100
4	DCE	55	100
5	Acetonitrile	100	100

Conditions: benzylalcohol 0.1 mmol, PhIO 0.25 mmol, catalyst 4 mg, solvent 2 mL, 25 °C, 4 h.

Table 7
Catalytic oxidation of benzylalcohol with different amount of catalyst of Quin-Ru-Quin

Entry	Catalyst (mg)	Conversion (%)	Selectivity (%)	Time required (h)
1	1.0	100	100	6.0
2	2.0	100	100	3.5
3	3.0	100	100	2.0
4	4.0	100	100	1.0

Conditions: benzylalcohol 0.1 mmol, PhIO 0.25 mmol, CH₃CN 2 mL, 25 °C.

3.2.2. The effect of the solvents

In order to select an efficient solvent, the oxidation was carried out in different solvents. The reactions were carried out at room temperature for 4 h. Several organic solvents were examined for the oxidation using Quin-Ru-Quin as catalyst. Table 6 shows that the reaction works in the selected organic medium. In dichloromethane, tetrahydrofuran, toluene, dichloroethane and acetonitrile, the conversion is 58%, 31%, 18%, 55% and 100%, respectively. Furthermore, in the all examined solvents the product selectivity remains 100%. The results indicate that the most efficient solvent for the oxidation is CH₃CN. In the following experiments, we chose acetonitrile as the organic medium to fulfill the oxidation.

3.2.3. The amount of catalyst

The reactions were carried out in acetonitrile at room temperature using Quin-Ru-Quin as catalyst. We changed the amount of the catalyst used to see the effect of the amount on the oxidation. When we use 4.0 mg of the Quin-Ru-Quin, only 1 h is needed to fulfill the oxidation. When we reduced the amount of the catalyst to a smaller amount, longer reaction time is needed to finish the oxidation under identical condition. The results are summarized in Table 7. We conclude that the amount of catalysts distinctly affected the oxidations.

Table 8
Catalytic oxidation of benzylalcohol by Quin-Ru-Quin with different amount of PhIO

Entry	PhIO consumption (mg (equiv.))	Conversion (%)	Selectivity (%)
1	0.011 (0.5)	27	100
2	0.022 (1.0)	57	100
3	0.033 (1.5)	77	100
4	0.044 (2.0)	96	100
5	0.055 (2.5)	100	100

Conditions: benzylalcohol 0.1 mmol, catalyst 4 mg, CH₃CN 2 mL, 25 °C, 1 h.

The oxidation results suggest that the use of 4.0 mg of catalyst will give full oxidation of benzylalcohol within the shortest time, so the appropriate amount of catalyst is 4.0 mg.

3.2.4. The amount of PhIO

In order to investigate the influence of the amount of the oxidant used on the reaction, the oxidations were carried out in acetonitrile at room temperature for 1 h using Quin-Ru-Quin as catalyst, the amount of PhIO we examined for the oxidation was ranged from 0.5 to 2.5 equiv. in the oxidations. The corresponding results with different amount of oxidant are concluded in Table 8.

With the use of 2.5 equiv. of PhIO, the substrate can be thoroughly oxidized in 1 h in the identical reaction condition. So the optimum amount of PhIO is 2.5 equiv. in the oxidation.

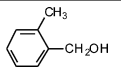
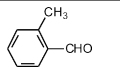
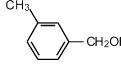
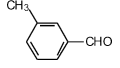
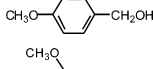
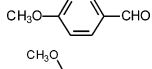
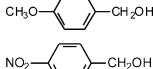
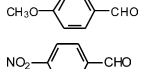
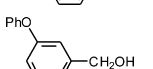
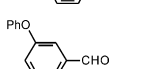
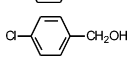
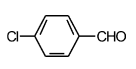
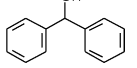
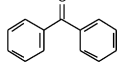
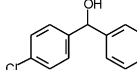
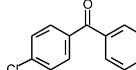
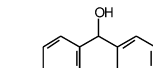
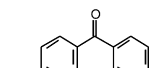
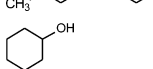
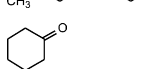
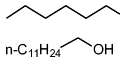
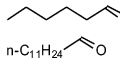
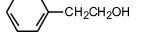
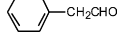
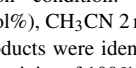
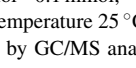
From all of the above investigation, we can conclude that the optimum reaction condition for the oxidation of benzylal-

cohol is $C_6H_5CH_2OH:PhIO = 1:2.5$ (mol/mol), catalyst 4 mg, $T = 25^\circ C$. The most efficient solvent is CH_3CN . The oxidation of other alcohols by all of the ruthenium complexes was undertaken according to the optimum reaction condition used for the oxidation of benzylalcohol except the variation of the reaction time due to different molecular structure of the alcohols.

3.3. Catalytic oxidation of other alcohols by the ruthenium complexes

The catalytic properties of the five-ruthenium complexes Phen-Ru-Phen, Phen-Ru-Quin, Phen-Ru-Bipy, Quin-Ru-Quin and Quin-Ru-Bipy for the oxidation of other alcohols were well investigated. It is found that all of the complexes are also active catalysts for the oxidations. With the catalysis of the complexes, many alcohols, including long-chain aliphatic alcohols, benzyl

Table 9
Catalytic oxidation of alcohols by the catalyst of Phen-Ru-Phen complex^a

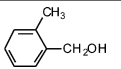
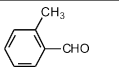
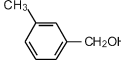
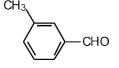
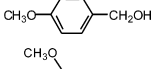
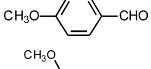
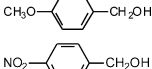
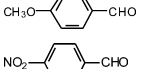
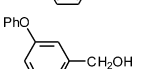
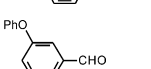
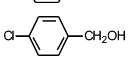
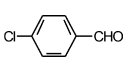
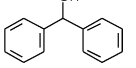
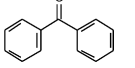
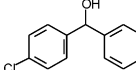
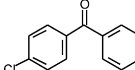
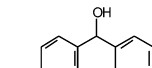
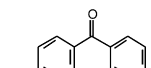
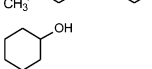
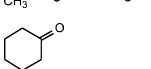
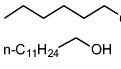
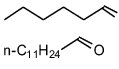
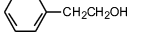
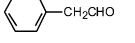
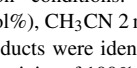
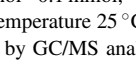
Run	Substrate	Product	Conversion (%) ^b	Time (h)	TON
1			100	4	32
2			100	4	32
3			100	4	32
4			100	6	32
5			100	4	32
6			100	4	32
7			98	8	31
8			63	8	20
9			74	8	23
10			73	8	23
11			73	8	23
12			100	4	32
13	$n-C_{11}H_{24}OH$	$n-C_{11}H_{24}CHO$	28	8	9
14			10	8	3

Reaction condition: alcohol 0.1 mmol, PhIO 2.5 equiv., catalyst 4 mg (3.2 mol%), CH_3CN 2 mL, temperature $25^\circ C$.

^a Products were identified by GC/MS analysis. Each of the oxidation bears the selectivity of 100%.

^b The conversion and the selectivity of each reaction were obtained by GC determination.

Table 10
Catalytic oxidation of alcohols by the catalysis of Phen-Ru-Bipy complex^a

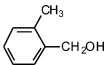
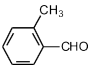
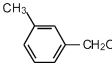
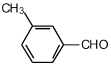
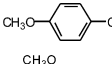
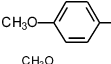
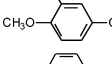
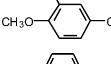
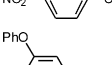
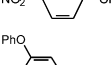
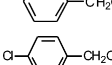
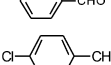
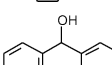
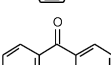
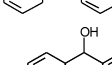
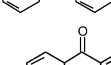
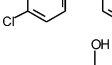
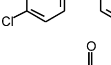
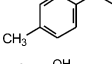
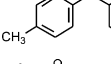
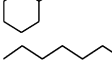
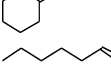
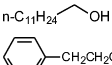
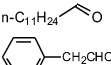
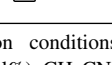
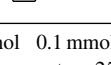
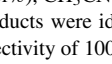
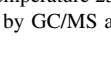
Run	Substrate	Product	Conversion (%) ^b	Time (h)	TON
1			77	8	14
2			100	2	18
3			100	2	18
4			100	4	18
5			100	2	19
6			100	2	19
7			89	8	17
8			63	8	12
9			80	8	15
10			73	8	14
11			59	8	11
12			100	6	19
13	$n-C_{11}H_{24}OH$	$n-C_{11}H_{24}CHO$	100	8	19
14			100	8	19

Reaction conditions: alcohol 0.1 mmol, PhIO 2.5 equiv., catalyst 4 mg (5.3 mol%), CH_3CN 2 mL, temperature $25^\circ C$.

^a Products were identified by GC/MS analysis. Each of the oxidation bears the selectivity of 100%.

^b The conversion and the selectivity of each reaction were obtained by GC determination.

Table 11
Catalytic oxidation of alcohols by the catalysis of Phen-Ru-Quin complex^a

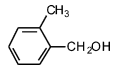
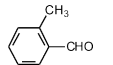
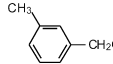
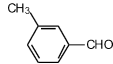
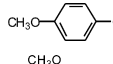
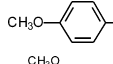
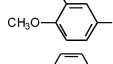
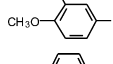
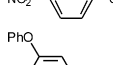
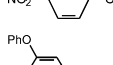
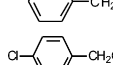
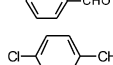
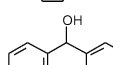
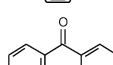
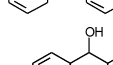
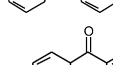
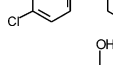
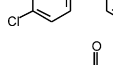
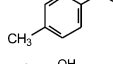
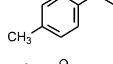
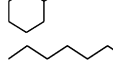
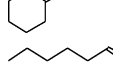
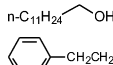
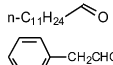
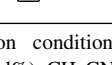
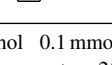
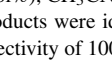
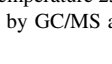
Run	Substrate	Product	Conversion (%) ^b	Time (h)	TON
1			100	3	17
2			100	3	17
3			100	0.5	17
4			100	1	17
5			100	1	17
6			100	0.5	17
7			88	8	15
8			60	8	10
9			89	8	15
10			77	8	13
11			63	8	11
12			100	6	17
13			85	8	14
14			40	8	7

Reaction conditions: alcohol 0.1 mmol, PhIO 2.5 equiv., catalyst 4 mg (6.0 mol%), CH₃CN 2 mL, temperature 25 °C.

^a Products were identified by GC/MS analysis. Each of the oxidation bears the selectivity of 100%.

^b The conversion and the selectivity of each reaction were obtained by GC determination.

Table 12
Catalytic oxidation of alcohols by the catalysis of Quin-Ru-Quin complex^a

Run	Substrate	Product	Conversion (%) ^b	Time (h)	TON
1			100	2	18
2			100	2	18
3			100	0.5	18
4			100	1	18
5			100	0.5	18
6			100	0.5	18
7			100	8	18
8			62	8	11
9			89	8	16
10			61	8	11
11			69	8	13
12			100	2	18
13			100	6	18
14			100	2	18

Reaction conditions: alcohol 0.1 mmol, PhIO 2.5 equiv., catalyst 4 mg (5.5 mol%), CH₃CN 2 mL, temperature 25 °C.

^a Products were identified by GC/MS analysis. Each of the oxidation bears the selectivity of 100%.

^b The conversion and the selectivity of each reaction were obtained by GC determination.

alcohols, benzhydrol and its derivatives can be easily oxidized to the corresponding carbonyl compounds under mild conditions. The results of these oxidations are summarized in Tables 9–13.

Through the comparison of the data of the oxidation results from Tables 9–13, we find the following conclusion.

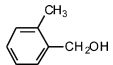
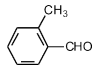
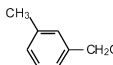
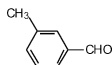
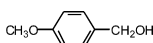
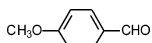
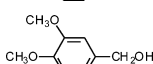
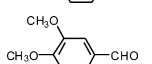
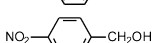
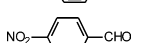
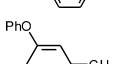
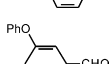
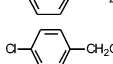
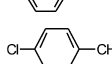
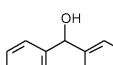
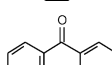
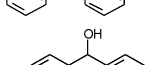
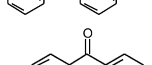
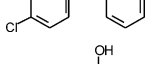
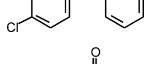
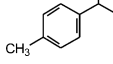
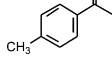
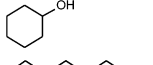
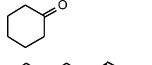
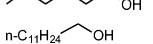
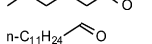
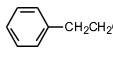
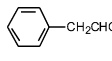
Complexes Phen-Ru-Phen (Table 9), Phen-Ru-Bipy (Table 10), Phen-Ru-Quin (Table 11), Quin-Ru-Quin (Table 12) and Bipy-Ru-Quin (Table 13) are active for the oxidation of alcohols, e.g. benzyl alcohols and their derivatives, benzhydrol and its derivatives, cyclic alcohols and long-chained aliphatic alcohols can be efficiently oxidized to the corresponding carbonyl compounds with the oxidant of PhIO under mild conditions. As we know, the aliphatic alcohols, especially those long-chained aliphatic alcohols are generally difficult to be oxidized under mild reaction conditions in other catalysis systems. Our results confirm that complexes Phen-Ru-Phen, Phen-Ru-Bipy, Phen-Ru-Quin, Quin-Ru-Quin and Bipy-Ru-Quin possess very

high catalytic activity for the oxidation of alcohols. Hence we conclude that this oxidation system is mild and efficient.

The oxidations using complexes Phen-Ru-Phen, Phen-Ru-Bipy, Phen-Ru-Quin, Quin-Ru-Quin and Bipy-Ru-Quin as catalyst bear the selectivity of 100%, that is, no products of further oxidation were detected. This means that these oxidation systems are useful for the formation of carbonyl compound. For the oxidation of benzyl alcohol and its derivatives, the oxidation system is excellent for the preparation of benzaldehyde and its derivatives from the corresponding alcohols.

Compared to other four complexes Phen-Ru-Phen, Phen-Ru-Bipy, Phen-Ru-Quin, and Bipy-Ru-Quin, complex Quin-Ru-Quin bears the highest catalytic activity for the oxidation (Table 12). We find that the system using Quin-Ru-Quin complex as catalyst needs shorter reaction time than the others under identical conditions. Furthermore, those complexes containing 8-hydroxy-quinoline portion have distinct reactivity. This may

Table 13
Catalytic oxidation of alcohols by the catalysis of Bipy-Ru-Quin complex^a

Run	Substrate	Product	Conversion (%) ^b	Time (h)	TON
1			100	8	21
2			100	4	21
3			100	2	21
4			100	4	21
5			100	2	21
6			100	2	21
7			90	8	19
8			57	8	12
9			61	8	13
10			58	8	12
11			71	8	15
12			100	4	21
13			100	8	21
14			100	8	21

Reaction conditions: alcohol 0.1 mmol, PhIO 2.5 equiv., catalyst 4 mg (4.7 mol%), CH₃CN 2 mL, temperature 25 °C.

^a Products were identified by GC/MS analysis. Each of the oxidation bears the selectivity of 100%.

^b The conversion and the selectivity of each reaction were obtained by GC determination.

owe to the ligand structure of the complexes. Among the three low molecular weight ligand, 1,10-phenanthroline possesses biggest molecular skeleton, as to 2,2'-bipyridine, the six membered ring can be circumrotated as the axial of the single C–C bond between the two rings, and which will affect the coordination processes. Whereas, the framework of 8-hydroxyquinoline is relatively small, it can be easily coordinated with the metal ion, which resulting in the more excellent catalytic activity for the oxidations.

As for the reaction properties of the selected alcohols, we can find it differs obviously. The benzyl alcohols have the highest reactivity in this system; however, the benzhydrol and its derivatives have the lowest. This is due to the molecular structure of the alcohols. The latter bears strong stereo hindrance for the contacting of the active site to the hydroxyl group, and this will decrease the conversion of the substrate during the oxidation.

4. Conclusions

Alcohols including benzyl alcohol and its derivatives, benzhydrol and its derivatives, cyclic alcohols and long-chained aliphatic alcohols were oxidized at room temperature in high conversion and 100% selectivity with iodosylbenzene catalyzed by ruthenium-containing complexes Phen-Ru-Phen, Phen-Ru-Bipy, Phen-Ru-Quin, Quin-Ru-Quin and Bipy-Ru-Quin. All of the oxidations give the desired products without further oxidation in this oxidation system. The complexes are very convenient to be prepared and the reaction condition is very mild.

Acknowledgements

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References

- [1] M. Hudlicky, *Oxidations in Organic Chemistry*, American Chemical Society, Washington, DC, 1990.
- [2] R.A. Sheldon, J.K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981, p. 350.
- [3] S.V. Ley, A. Madin, in: B.M. Trost, I. Fleming (Eds.), *Comprehensive Organic Synthesis*, vol. 7, Pergamon, Oxford, 1991, p. p. 251.
- [4] G. Cainelli, G. Cardillo, *Chromium Oxidations in Organic Chemistry*, Springer, Berlin, 1984.
- [5] S.V. Ley, A. Madin, in: B.M. Trost, I. Fleming (Eds.), *Comprehensive Organic Synthesis*, vol. 7, Pergamon, Oxford, 1991, p. p. 291.
- [6] R. Ghorbani-Vaghei, A. Khazaei, *Tetrahedron Lett.* 44 (2003) 7525.
- [7] J.S. Yadav, B.V.S. Reddy, A.K. Basak, A.V. Narsaiah, *Tetrahedron* 60 (2004) 2131.
- [8] W.J. Chung, D.K. Kim, Y.S. Lee, *Tetrahedron Lett.* 44 (2003) 9251.
- [9] X.J. Meng, K.F. Lin, X.Y. Yang, Z.H. Sun, D.Z. Jiang, F.S. Xiao, *J. Catal.* 218 (2003) 460.
- [10] G. Ferguson, A.N. Ajjou, *Tetrahedron Lett.* 44 (2003) 9139.
- [11] R. Naik, P. Joshi, R.K. Deshpande, *Catal. Commun.* 5 (2004) 195.
- [12] F. Zaera, *Catal. Today* 81 (2003) 149.
- [13] K.O. Xavier, J. Chacko, K.K. Mohammed Yusuff, *J. Mol. Catal. A Chem.* 178 (2002) 275.
- [14] S. Das, T. Punniyamurthy, *Tetrahedron Lett.* 44 (2003) 6033.
- [15] I. Fernández, J.R. Pedro, A.L. Roselló, R. Ruiz, I. Castro, X. Ottenwealder, *Y. Journaux, Eur. J. Org. Chem.* (2001) 1235.
- [16] V.B. Sharma, S.L. Jain, B. Sain, *Tetrahedron Lett.* 44 (2003) 383.
- [17] J.E. Remias, A. Sen, *J. Mol. Catal. A Chem.* 189 (2002) 33.
- [18] Y. Shvo, V. Goldman-Lev, *J. Organomet. Chem.* 650 (2002) 151.
- [19] T.L. Stuchinskaya, I.V. Kozhevnikov, *Catal. Commun.* 4 (2003) 417.
- [20] J. Brinksma, M.T. Rispens, R. Hage, B.L. Feringa, *Inorg. Chim. Acta* 337 (2002) 75.
- [21] M. Bagherzadeh, *Tetrahedron Lett.* 44 (2003) 8943.
- [22] A. Wolfson, S. Wuyts, D.E. De Vos, I.F.J. Vankelecom, P.A. Jacobs, *Tetrahedron Lett.* 43 (2002) 8107.
- [23] A.L.B. Marques, W.H. Li, E.P. Marques, J.J. Zhang, *Electrochim. Acta* 49 (2004) 879.
- [24] K. Ebitani, H.B. Ji, T. Mizugaki, K. Kaneda, *J. Mol. Catal. A Chem.* 212 (2004) 161.
- [25] Z.Q. Lei, Q.X. Kang, X.Z. Bai, Z.W. Yang, Q.H. Zhang, *Chin. Chem. Lett.* 16 (2005) 846.
- [26] Q.X. Kang, J.J. Luo, X.Z. Bai, Z.W. Yang, Z.Q. Lei, *J. Organomet. Chem.* 690 (2005) 6309.
- [27] C.R. Leidner, R.W. Murray, *J. Am. Chem. Soc.* 106 (1984) 1606.
- [28] J. Pebler, *Inorg. Chem.* 22 (1983) 4125.