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ROYAL SOCIETY OF CHEMISTRY

rsc.li/njc

View Article Online
DOI: 10.1039/C8NJ00329G

Journal Name

ARTICLE

Received 00th January 20xx,

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Ruthenium Carbonyl Complexes with Pyridylalkanol Ligands: Synthesis, Characterization and Catalytic Properties for Aerobic Oxidation of Secondary Alcohol

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Reaction of $Ru_3(CO)_{12}$ with pyridylalkanol ligands $PyC(CH_2)_4OH$ (**L**^{1}H), $PyC(CH_2)_5OH$ (**L**^{2}H) and $PyCR^1R^2OH$ ($R^1 = R^2 = CH_3$ (**L**^{3}H); $R^1 = CH_3$, $R^2 = C_6H_5$ (**L**^{4}H); $R^1 = H$, $R^2 = C_6H_5$ (**L**^{5}H); $R^1 = H$, $R^2 = 4\text{-}CH_3C_6H_4$ (**L**^{6}H); $R^1 = H$, $R^2 = 4\text{-}OMeC_6H_4$ (**L**^{7}H); $R^1 = H$, $R^2 = 4\text{-}ClC_6H_4$ (**L**^{8}H); $R^1 = H$, $R^2 = 4\text{-}BrC_6H_4$ (**L**^{9}H); $R^1 = H$, $R^2 = 4\text{-}CF_3C_6H_4$ (**L**^{10}H)) in refluxing xylene afforded the bis-chelate rhenium carbonyl complexes $[(L^n)_2Ru_3(CO)_8]$ (*n* =1 (**1a**); *n* = 2 (**1b**); *n* = 3 (**1c**); *n* = 4 (**1d**); *n* = 5 (**1e**); *n* = 6 (**1f**); *n* = 7 (**1g**); *n* = 8 (**1h**); *n* = 9 (**1i**); *n* = 10 (**1j**)), respectively. All the novel rhenium complexes were fully characterized by NMR, elemental analyses and IR spectra and the molecular structures of **1a**, **1c, 1e**, **1g** and **1i** were further determined by single crystal X-ray diffraction analysis. In the presence of TEMPO (TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxyl), these trirhenium carbonyl clusters displayed high reactivity for aerobic oxidation of secondary alcohols to give the corresponding ketonic compounds in good to excellent yield using ambient air as the source of oxidant.

Introduction

Transition-metal-catalyzed protocols have been designed for a variety of organic synthesis.[1-5] The oxidation of alcohols to corresponding aldehydes and ketones assisted by transition metal catalysts has garnered tremendous attention because of their profound importance in synthetic organic chemistry.[6-9] Traditionally, these reactions usually performed with excess inorganic or organic oxidants–often hazardous or toxic–such as chromium(VI) oxide,[10] hypochlorite,[11] manganese oxide,[12] which limited their applications in large scale syntheses. Recently, the employment of molecular oxygen[13] or hydrogen peroxide[14] as oxidant has attracted widespread interest in alcohol oxidation reactions in the view of environmental and economic concerns. Several homogeneous catalytic systems, e.g., ruthemiun,[15] iridium,[16] manganese[17] complexes and heterogeneous catalytic systems including cobalt,[18] rhodium[19] and other metal catalysts[20,21] have been applied in oxidation of alcohols. For instance, Yu and co-workers presented an acceptorless dehydrogenation of alcohols for synthesis ketones catalyzed by dimeric pincer-Ru complex.[22] This catalyst showed high catalytic activity for oxidantion of secondary alcohols with diverse functionalities. However, copious amounts of base were necessary for good conversion over more than 20 hours. More recently, Jones reported a Cp^*Rh-catalyzed dehydrogenative oxidation of 1-phenylethanol to afford acetophenone in >99% yield.[23] While the Cp^*Rh complex was sensitive to moisture and reaction temperature was up to 150 °C. Thus, it is important to develop new catalytic system which can be proceeded under mild condition and is east to implement. In addition to metallocenes or metal chlorides compounds, an alternative approach is to use simple and air/moisture stable metal carbonyl compounds, especially ruthenium carbonyl complexes to accomplish chemical transformations.[24] In recent years, some examples of ruthenium carbonyl complexes were synthesized for promoting chemical reactivity for oxidation of alcohols.[12b,25] Whereas the progress of using ruthenium carbonyl cluster compounds bearing suitable ligands as catalysts for alcohol oxidation is sluggish. As known, ligands in the catalytic systems can not only solubilize the transition-metal complexes in organic media but also adjust the redox potential of metal center for appropriate reactivity. Thus, various of ligands such as arylazo phenolate,[26] bipyridine,[27] and pincer[28] were investigated to support metal complexes, in which *O,N*-dentate ligands have drawn major attention. For example, Ding's group reported that the L-Proline could act as a efficient *O,N*-bidentate ligand to promote aerobic oxidation of all classes of alcohol substrates with high selectivity in combination of CuI.[29] Besides, pyridylalkanol compound which feature strong donor power, broad solubility and rigid binding was also one of efficient *O,N*-dentate ligands. Therefore, the alcohol oxidation catalyzed by ruthenium carbonyl clusters

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†Electronic Supplementary Information (ESI) available: Includes X-ray crystallographic data and refinements for complexes **1a**, **1c**, **1e**, **1g** and **1i** in CIF format, summary of crystallographic data, the optimization of benzene ethanol using different oxidants and NMR spectra of products. See DOI: 10.1039/x0xx00000x

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DOI: 10.1039/C8NJ00329G

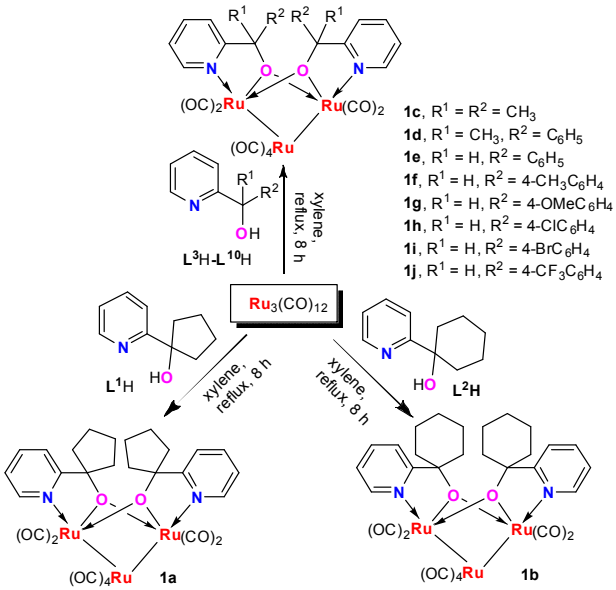
bearing pyridylalkanol ligands under mild conditions is worthy of being evaluated.

On the basis of above premises, together with the aim to develop a efficient catalytic system, we became interested in investigating the complexes composed of transition metal carbonyls and various pyridine alkoxide derivatives and their applications in organic transformations. Herein, we report the synthesis and characterization of a series of trinuclear ruthenium clusters compounds bearing pyridylalkanol ligands. Further, this kind of compounds was active to catalyze oxidation of secondary alcohols to form corresponding ketones with oxygen (air) as oxidant.

Results and discussion

Synthesis and characterization of the ruthenium carbonyl complexes

Thermal treatment of the pyridylalkanol ligands $PyC(CH_2)_4OH$ ($\mathbf{L^1}H$), $PyC(CH_2)_5OH$ ($\mathbf{L^2}H$) and $PyCR^1R^2OH$ ($R^1 = R^2 = CH_3$ ($\mathbf{L^3}H$); $R^1 = CH_3$, $R^2 = C_6H_5$ ($\mathbf{L^4}H$); $R^1 = H$, $R^2 = C_6H_5$ ($\mathbf{L^5}H$); $R^1 = H$, $R^2 = 4\text{-}CH_3C_6H_4$ ($\mathbf{L^6}H$); $R^1 = H$, $R^2 = 4\text{-}OMeC_6H_4$ ($\mathbf{L^7}H$); $R^1 = H$, $R^2 = 4\text{-}ClC_6H_4$ ($\mathbf{L^8}H$); $R^1 = H$, $R^2 = 4\text{-}BrC_6H_4$ ($\mathbf{L^9}H$); $R^1 = H$, $R^2 = 4\text{-}CF_3C_6H_4$ ($\mathbf{L^{10}}H$)) in refluxing xylene afforded the bis-chelate rhenium carbonyl complexes$[(\mathbf{L}^n)_2Ru_3(CO)_8]$ (n = 1 (**1a**); n = 2 (**1b**); n = 3 (**1c**); n = 4 (**1d**); n = 5 (**1e**); n = 6 (**1f**); n = 7 (**1g**); n = 8 (**1h**); n = 9 (**1i**); n = 10 (**1j**)), respectively in 63 ~ 81% yield, as shown in Scheme 1.



Scheme 1 Synthesis of ruthenium carbonyl complexes.

All the new complexes **1a-1j** were characterized by ^1H and ^{13}C NMR spectroscopy along with elemental analyses. In the ^1H NMR spectra of these complexes, the O*H* signals around 5.1 ~ 5.6 ppm disappeared with respect to those in the free ligands, indicating the deprotonation of the ligands and the coordination of the hydroxyl groups to the metal centers. In the aliphatic region, the alkyl or *H* resonances on bridge-methine were slightly shifted to upfield for all the complexes. Specially, the signals of alkyl groups in free ligands $\mathbf{L^1}H$ ~ $\mathbf{L^3}H$ were split into two sets compared to those in complexes **1a** ~ **1c** respectively, which suggested that the alkyl groups on bridge-methine were diastereotopic and in different chemical environments. The IR spectra of all triruthenium complexes exhibited three or four absorption bands at 1910 ~ 2080 cm^{-1} due to the presence of several types of terminal carbonyl. In IR spectra of free pyridylalkanol ligands, the characteristic ν(OH) bonds at 3185 ~ 3435 cm^{-1} disappeared on complexation with $Ru_3(CO)_8$, indicating the deprotonation of the hydroxyl groups and coordination of pyridylalkanol ligands to ruthenium atoms.

X-ray diffraction studies

The molecular structures of complexes **1a**, **1c**, **1e**, **1g** and **1i** were determined by single-crystal X-ray diffraction analysis. The crystals that are suitable for X-ray structural determination were grown from a CH_2Cl_2/hexane mixed solvent system. Their molecular structures at a 30% (**1g** 10%) probability level are illustrated in Fig. 1−5 with selected bond distances and angles in the captions, respectively. The crystallographic data of all these compounds is given in the electronic supplementary information. The X-ray diffraction analysis reveals that all these compounds are isostructural, which is triruthenium cluster accompanied by two pyridylalkoxo ligands simultaneously coordinated to two ruthenium atoms with μ–O atom acting as a three-electron donor. In these molecules, three ruthenium atoms form an isosceles triangle with two strong Ru–Ru distances in the range of 2.76 ~ 2.79 Å, which are slightly shorter than those in $Ru_3(CO)_{12}$ (2.85 Å)[30] and similar to those of 2.74 Å and 2.75 Å in $Ru_3(CO)_8(\mu\text{-}OC_6H_4POMe\text{-}2)$ complex[31] and one of longer weak Ru-Ru distance (3.00 ~ 3.04 Å). The Ru–N distances (2.15 ~ 2.19 Å) in these complexes are in agreement with those of 2.14 Å, 2.16 Å observed in $Ru_3(CO)_8[C_9H_6NO]_2$,[32] while the distances between ruthenium atom and bonding hydroxyl oxygen (2.07 ~ 2.09 Å) were obviously shorter than those of 2.19 Å, 2.18 Å in above 8-quinolinol triruthenium complex[32] and those of 2.13 Å, 2.14 Å in $[PyCH{=}C(Ph)O]_2Ru_3(CO)_8$.[33] The angle between two ruthenium atoms and oxygen, that is Ru(1)-O1-Ru(2/1i), ranging from 90.50° to 91.81° are comparable to those in $Ru_3(CO)_8[C_9H_6NO]_2$ and $[PyCH{=}C(Ph)O]_2Ru_3(CO)_8$ (89.91°, 89.64° and 90.78°, 90.78°, respectively).

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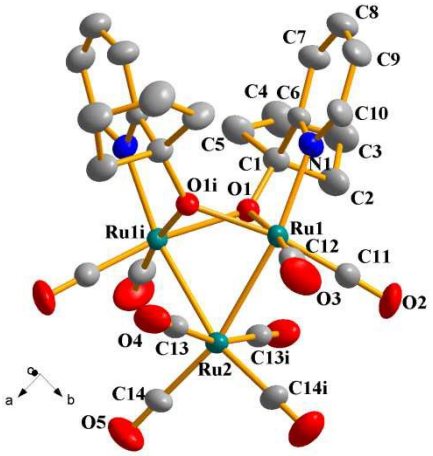

Fig. 1 Perspective view of **1a** with thermal ellipsoids drawn at 30% probability level. Hydrogens are omitted for clarity. The selected bond lengths (Å) and angles (deg.): Ru(1)-N(1) 2.158(5), Ru(1)-O(1) 2.076(4), Ru(1)-Ru(2) 2.7722(8), Ru(2)-Ru(1i) 2.7722(8), Ru(1)-C(11) 1.828(8); C(11)-Ru(1)-N(1) 97.8(3), O(1)-Ru(1)-N(1) 76.71(19), Ru(1i)-Ru(2)-Ru(1) 65.69(3), O(1)-Ru(1)-Ru(2) 83.82(11), Ru(1)-O(1)-Ru(1i) 90.76(15), N(1)-Ru(1)-Ru(2) 160.43(16).

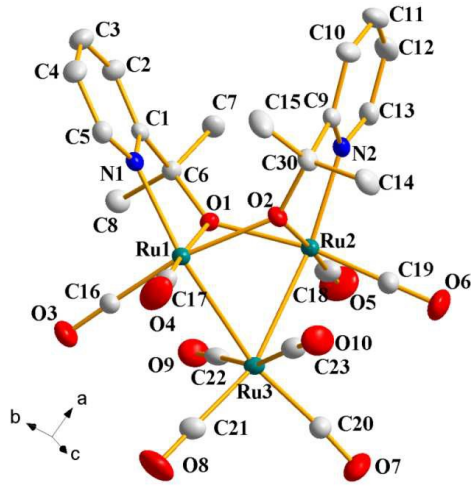

Fig. 2 Perspective view of **1c** with thermal ellipsoids drawn at 30% probability level. Hydrogens are omitted for clarity. The selected bond lengths (Å) and angles (deg.): Ru(1)-N(1) 2.171(3), Ru(2)-N(2) 2.169(3), Ru(1)-O(1) 2.076(3), Ru(2)-O(2) 2.081(3), Ru(1)-Ru(3) 2.7934(4), Ru(2)-Ru(3) 2.7980(4); C(17)-Ru(1)-N(1) 101.93(15), O(1)-Ru(1)-N(1) 77.24(10), Ru(1)-Ru(3)-Ru(2) 65.881(11), C(18)-Ru(2)-N(2) 102.73(16), O(2)-Ru(2)-N(2) 76.89(11), O(1)-Ru(2)-Ru(3) 82.70(6), Ru(1)-O(1)-Ru(2) 91.55(10).

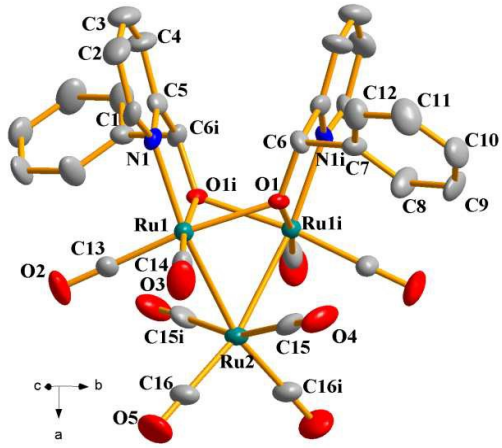

Fig. 3 Perspective view of **1e** with thermal ellipsoids drawn at 30% probability level. Hydrogens are omitted for clarity. The selected bond lengths (Å) and angles (deg.): Ru(1)-N(1) 2.149(8), Ru(1)-O(1i) 2.095(6), Ru(1)-Ru(2) 2.7658(14), Ru(2)-Ru(1i) 2.7658(14); C(13)-Ru(1)-N(1) 97.0(4), O(1i)-Ru(1)-N(1) 78.0(3), Ru(1i)-Ru(2)-Ru(1) 66.22(5), Ru(1i) -O(1)-Ru(1) 90.5(2), N(1)-Ru(1)-Ru(2) 161.5(2), C(13)-Ru(1)-O(1i) 100.0(4).

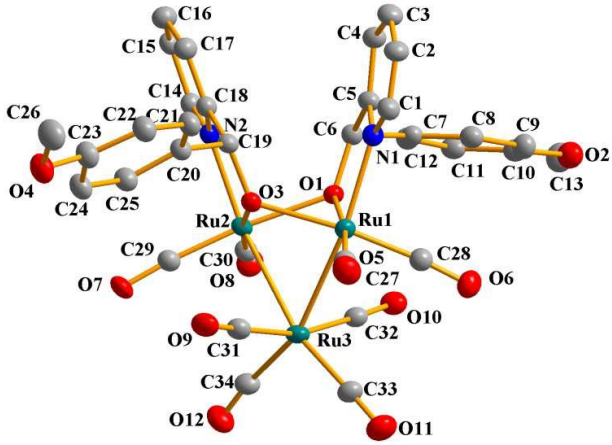

Fig. 4 Perspective view of **1g** with thermal ellipsoids drawn at 10% probability level. Hydrogens are omitted for clarity. The selected bond lengths (Å) and angles (deg.): Ru(1)-N(1) 2.137(17), Ru(2)-N(2) 2.133(15), Ru(1)-Ru(3) 2.766(2), Ru(2)-Ru(3) 2.764(2), Ru(1)-O(1) 2.072(9), Ru(2)-O(3) 2.075(11); C(28)-Ru(1)-N(1) 96.0(8), O(1)-Ru(1)-N(1) 78.0(7), Ru(3)-Ru(2)-Ru(1) 57.19(5), C(29)-Ru(2)-N(2) 95.7(8), O(3)-Ru(2)-N(2) 78.1(6), O(3)-Ru(1)-Ru(3) 82.5(3), Ru(1)-O(1)-Ru(2) 91.6(4).

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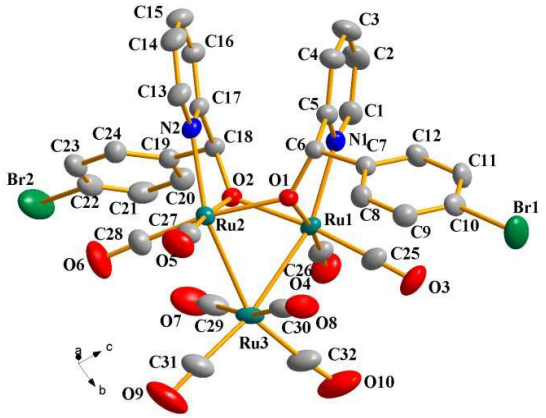
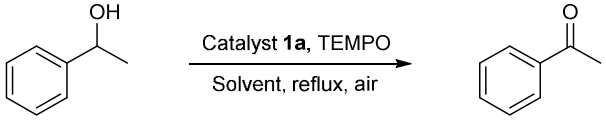


Fig. 5 Perspective view of **1i** with thermal ellipsoids drawn at 30% probability level. Hydrogens are omitted for clarity. The selected bond lengths (Å) and angles (deg.): Ru(1)-N(1) 2.190(5), Ru(2)-N(2) 2.190(5), Ru(2)-Ru(3) 2.7837(7), Ru(1)-Ru(3) 2.7827(7), Ru(1)-O(1) 2.083(3), Ru(2)-O(2) 2.081(3); C(25)-Ru(1)-N(1) 100.5(2), O(1)-Ru(1)-N(1) 77.15(16), Ru(1)-Ru(3)-Ru(2) 65.947(17), C(27)-Ru(2)-N(2) 105.0(2), O(1)-Ru(2)-Ru(3) 81.13(9), Ru(1)-O(1)-Ru(2) 91.39(13).

Catalytic oxidation of alcohols

All the new triruthenium carbonyl complexes beaing electronic and steric environment of the pyridylalkanol ligands were evaluated as catalysts for aerobic oxidation of secondary alcohols in the presence of TEMPO as co-oxidant. We set out to screen various reaction conditions using benzene ethanol as model substrate. The results are summarized in Table 1. When using complex **1a** (2.5 mol%) as catalyst, acetophenone was achieved in moderate yield in the presence of NMO/Bu^{t}OOH/H_2O_2 as oxidants (see Table S1) and toluene as solvent. The yield of desired product was improved to 71% by using air as oxidant in the presence of TEMPO (Table 1, entry 1). With the increase of catalyst loading from 2.5 mol% to 4.0 mol%, the acetophenone gradually increased and up to 78% yields was obtained.

Table 1 Benzene ethanol aerobic oxidation catalyzed by complex 1a[a]

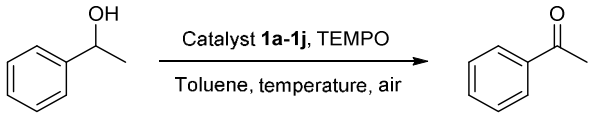


Entry	Catalyst (mol%)	Solvent	Yield (%)[b]
1	2.5	toluene	71
2	3.0	toluene	77
3	4.0	toluene	78
4	3.0	xylene	71
5	3.0	CH_2Cl_2	68
6	3.0	CH_3CN	62
7	3.0	DMF	65
8[c]	3.0	toluene	70
9[d]	3.0	toluene	78
10[e]	3.0	toluene	76
11[f]	3.0	toluene	77
12	—	toluene	8
13[g]	3.0	toluene	46
14[h]	$Ru_3(CO)_{12}$	toluene	29

[a]Reaction conditions: benzene ethanol (1.0 mmol), solvent (5.0 mL), TEMPO (10.0 mol%), reaction time 6 h. [b]Isolated yield based on substrate. [c]Reaction time, 4 h. [d]Reaction time, 10 h. [e]Bu^{t}OK (1.0 mmol) was employed. [f]Na_2CO_3 (1.0 mmol) was employed. [g]TEMPO was omitted. [h]$Ru_3(CO)_{12}$ (3.0 mol%).

The effect of the solvents on oxidation reaction was also investigated. As shown in Table 1, xylene, CH_3CN and DMF give the acetophenone with only 71%, 62% and 65% yields after 6 h, respectively (Table 1, entries 4, 6, 7). In low boiling point solvent, that is in CH_2Cl_2, the present catalytic system showed approximately the same activity compared to $[Ru(CO)_2(L)(Cl)_2]$(L = thioether-containing azo-phenol)/NMO catalytic system.[34] Among solvents, toluene was a better solvent to give the desired product in 77% yield. The employment of bases, e.g., Na_2CO_3, Bu^{t}OK to the reaction media showed little influence on catalytic activity and the yields remained almost unchanged compared with the catalytic system without using base (Table 1, entries 2, 10 and 11). Finally, the control experiments showed that trace amount of acetophenone was detected in the absence of **1a** and only 46% yield was obtained when **1a** was used alone without any oxidants. To compared with complex **1a**, $Ru_3(CO)_{12}$ was also tested as catalyst to oxidant benzene ethanol to gave target product in only 29% yields under the same condition, indicating that pyridylalkoxo ligand in complex **1a** play a key role toward the increasing of catalytic activity for alcohols oxidation.

Table 2. Benzene ethanol aerobic oxidation catalyzed by complexes 1a-1j[a]



Entry	Catalyst	Temp (°C)	Yield (%)[b]
1	**1a**	90	61
2	**1a**	60	43
3	**1b**	110	74
4	**1c**	110	72
5	**1d**	110	70
6	**1e**	110	84
7	**1f**	110	68
8	**1g**	110	71
9	**1h**	110	82
10	**1i**	110	80
11	**1j**	110	79

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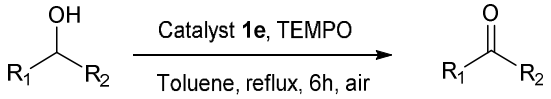
DOI: 10.1039/C8NJ00329G

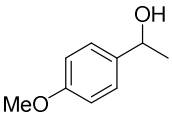
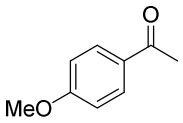
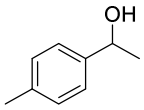
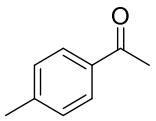
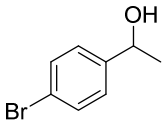
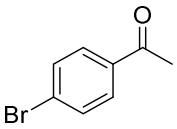
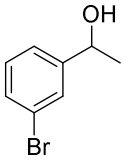
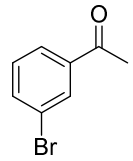
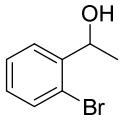
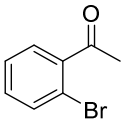
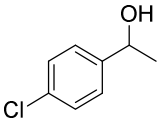
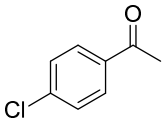
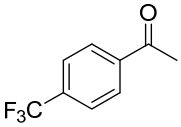
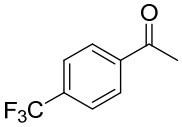
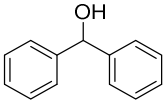
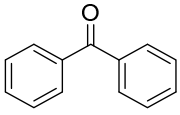
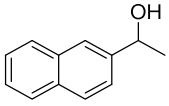
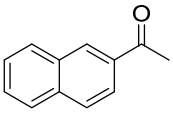
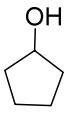
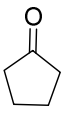
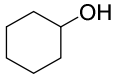
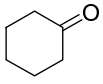
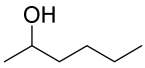
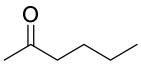
[a]Reaction conditions: benzene ethanol (1.0 mmol), cat. (3.0 mol%), toluene (5.0 mL), TEMPO (10.0 mol%), reaction time 6 h. [b]Isolated yield based on substrate.

In continuation of the optimization, the effect of reaction temperature on the reactivity was further investigated. When reaction temperature was reduced from 110 °C to 60 °C, a remarkable decrease in the yield of carbonyl compound was observed, which indicating the temperature played a pivotal role in promoting the catalytic process. Thus, the optimized reaction conditions: alcohol (1.0 mmol), catalyst (3.0 mol%) and TEMPO (10.0 mol%) under air in refluxing toluene (5 mL) were established. We then examined the catalytic oxidation of benzene ethanol using ruthenium carbonyl catalysts bearing several of α-substituted pyridylalkoxo ligands. As seen from Table 2, all ten complexes displayed moderate to good catalytic activity, the yields of acetophenone falling in the range of 68%~84% (Table 2, entries 5-11). At 110 °C, the activities decreased in the order **1e** (R = C_6H_5) **>1h** (R = 4-ClC_6H_5) **>1i** (R = 4-BrC_6H_5) **>1j** (R = 4-$CF_3C_6H_5$) **>1a** (R = cyclopentyl) **>1b** (R = cyclohexyl) **>1c** (R = $(Me)_2$) **>1g** (R = 4-OMeC_6H_5) **>1d** (R = C_6H_5, Me) **>1f** (R = 4-MeC_6H_5). These results suggested that pyridylalkanol ligands can alter the catalytic activity of complexes owing to steric and electronic properties provided by various substituents. Thus, the catalyst **1e** bearing suitable electronic effect (compared to **1a**, **1b** and **1f-1j**) and steric hindrance (compared to **1c** and **1d**) ligand showed highest activity, giving the target product in 84% yield.

To explore the scope of substrates, a diverse array of secondary alcohols that contained functional groups were conducted using **1e** as catalyst under optimized conditions. The results are summarized in Table 3. The 1-arylethanols bearing electron-donating and -withdrawing groups at aromatic ring oxidized smoothly to give the corresponding acetophenone derivatives in good to excellent yields (Table 3, entries 1-7). Methoxy-, chloro-, bromo-, trifluoromethyl-substituents were tolerated in this catalytic system. Gratifyingly, the sterically hindered alcohols, i.e., diphenylmethanol and 2-naphthylmethanol, also proceeded to give the corresponding ketones in high yield (Table 3, entries 8, 9). The aliphatic cyclic and linear secondary alcohols, that are cyclopentanol, cyclohexanol and2-Hexanol were converted to corresponding ketones in slightly lower yields (78%, 67%, 74%, respectively) compared to aromatic secondary alcohols. This reason arose from the substantially less acidic α-C–H bonds of aliphatic alcohols, leading to slower C–H cleavage than those aromatic substrates.[35]

Table 3. Aerobic oxidation of various secondary alcohols catalyzed by 1e[a]



Entry	Substrate	Product	yield (%)[b]
1			91
2			92
3			82
4			84
5			81
6			85
7			87
8			91
9			80
10[c]			78[d]
11[c]			67[d]
12[c]			74[d]

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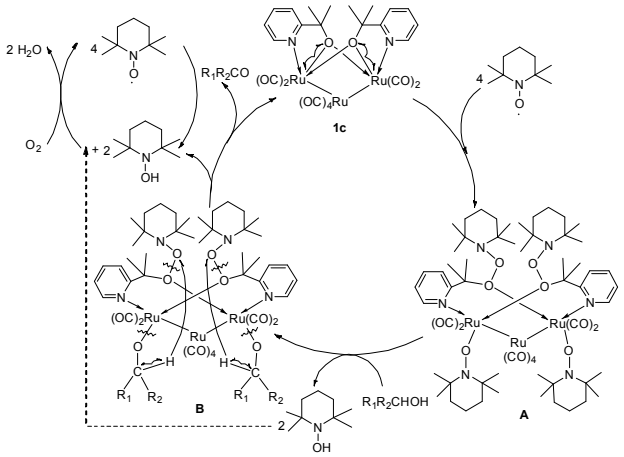
[a]Reaction conditions: benzene ethanol (1.0 mmol), cat. (3.0 mol%), toluene (5 mL), TEMPO (10.0 mol%). [b]Isolated yield based on substrate. [c]Reaction time, 15 h. [d]Determined by GC with area normalization method.



Scheme 2 A plausible mechanism for trinuclear ruthenium carbonyl complex **1c**/TEMPO catalyzed alcohol oxidation.

On the basis of our preliminary data and precedent Ru-catalyzed oxidation processes,[11b,38] a plausible mechanism for oxidation of alcohols catalyzed by representative complex **1c** is shown in Scheme 2. The first step of reaction would involve homolysis of Ru-O bond of complex **1c** in the presence of TEMPO to afford complex **A**, in which TEMPO moiety connected to Ru and oxygen atoms, respectively. Then the reaction of complex **A** with alcohol to give intermediate **B** accompanied by release of two molecules of TEMPOH. Subsequent cleavage of C-H, Ru-O and O-O bonds in species **B** occurred and a hydrogen radical was abstracted by the released TEMPO to afford another two molecules of TEMPOH, a ketone product and complex **1c**. Finally, the TEMPOH are oxidized by oxygen to regenerate TEMPO.

Conclusions

In summary, we have used a number of bidentate pyridylalkanol ligands **L** to form new ruthenium carbonyl complexes, namely $[(\mathbf{L})_2Ru_3(CO)_8]$ *via* the precursor $Ru_3(CO)_{12}$. All these bis-chelate ruthenium complexes were synthesized in high yields in refluxing xylene and well characterized by NMR, elemental analyses etc. The structures of several typical complexes were further confirmed by single crystal X-ray diffraction. These new trinuclear ruthenium clusters exhibited high catalytic activity and broad functional group compatibility for aerobic oxidant of secondary alcohols using ambient air as oxidant, which made catalytic procedure simple and easily handled. To the best of our knowledge, the present catalytic process is the first example of aerobic oxidation of alcohols using trinuclear ruthenium carbonyl complexes/TEMPO system.

Experimental section

General considerations

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified argon using standard Schlenk or drybox techniques. Chemical reagents were purchased from commercial sources and used as received. All the solvents were dried and distilled under nitrogen prior to use by standard methods. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III-500 NMR spectrometer at room temperature in $CDCl_3$. IR spectra were recorded as KBr disks on a Thermo Fisher is 50 spectrometer and elemental analyses were performed on a Vario EL III analyzer. Pyridine alcohol ligands $\mathbf{L}^1$H ~ $\mathbf{L}^{10}$H, that are α-substituted 2-pyridylmethanols, were prepared according to the literature methods.[36, 37]

Syntheses of the and complexes

Synthesis of 1a A solution of $\mathbf{L}^1$H (0.230 g, 1.408 mmol) and $Ru_3(CO)_{12}$ (0.300 g, 0.469 mmol) in 25 mL of toluene was heated at reflux for 8h. After the mixture was cooled to ambient temperature, the solvent was removed under reduced pressure and the residue was placed in an Al_2O_3 column. Elution with ethyl acetate/petroleum ether to give **1a** as brown orange crystals (yield 0.325 g, 81.3%). Anal. Calc. for $C_{28}H_{24}N_2O_{10}Ru_3$: C, 39.49; H, 2.84; N, 3.29. Found (%): C, 39.59; H, 2.97; N, 3.11; ^{1}H NMR (ppm in $CDCl_3$, 500 MHz): δ 1.21-1.27 (m, 4H, CH_2), 1.43-1.57 (m, 4H, CH_2), 1.74-1.95 (m, 4H, CH_2), 2.06-2.18 (m, 4H, CH_2), 6.64 (d, J = 8.0 Hz, 2H, Py-H), 7.16 (t, J = 6.0 Hz, 2H, Py-H), 7.54 (t, J = 7.5 Hz, 2H, Py-H), 8.78 (d, J = 5.5 Hz, 2H, Py-H). ^{13}C NMR (ppm in $CDCl_3$, 125 MHz): δ 24.8, 27.5, 42.7, 46.8, 97.3, 118.6, 122.2, 137.4, 152.6, 172.3, 193.9, 204.1, 204.3, 206.7. IR (υ_{CO}, KBr, cm^{-1}): 1909 (s), 1986 (s), 2067 (s).

Synthesis of 1b Complex **1b** was synthesized in the same way as described above for the synthesis of **1a** using $\mathbf{L}^2$H (0.249 g, 1.408 mmol) and $Ru_3(CO)_{12}$ (0.300 g, 0.469 mmol). Complex **1b** was obtained as brown orange crystals (yield 0.238 g, 79.6%). Anal. Calc. for $C_{30}H_{28}N_2O_{10}Ru_3$: C, 40.96; H, 3.21; N, 3.18. Found (%): C, 41.14; H, 3.34; N, 3.30; ^{1}H NMR (ppm in $CDCl_3$, 500 MHz): δ 1.38-1.54 (m, 14H, CH_2), 2.07-2.21 (m, 6H, CH_2), 7.31 (t, J = 5.0 Hz, 2H, Py-H), 7.51 (d, J = 7.5 Hz, 2H, Py-H), 7.88 (t, J = 8.0 Hz, 2H, Py-H), 8.81 (d, J = 5.5 Hz, 2H, Py-H). ^{13}C NMR (ppm in $CDCl_3$, 125 MHz): δ 22.1, 23.0, 26.1, 36.0, 42.5, 88.8, 121.7, 122.6, 137.1, 150.8, 174.0, 194.4, 203.6, 203.7, 206.6. IR (υ_{CO}, KBr, cm^{-1}): 1921 (s), 1972 (s), 2050 (s).

Synthesis of 1c Complex **1c** was synthesized in the same way as described above for the synthesis of **1a** using $\mathbf{L}^3$H (0.282 g, 1.408 mmol) and $Ru_3(CO)_{12}$ (0.300 g, 0.469 mmol) (yield 0.236 g, 62.8%). Anal. Calc. for $C_{24}H_{20}N_2O_{10}Ru_3$: C, 36.05; H, 2.52; N, 3.50. Found (%): C, 36.17; H, 2.40; N, 3.37; ^{1}H NMR (ppm in $CDCl_3$, 500 MHz): δ 1.00 (s, 6H, CH_3), 1.34 (s, 6H, CH_3), 6.92 (d, J = 8.5 Hz, 2H, Py-H), 7.16 (t, J = 6.5 Hz, 2H, Py-H), 7.59 (t, J = 8.0 Hz, 2H, Py-H), 8.73 (d, J = 5.0 Hz, 2H, Py-H). ^{13}C NMR (ppm in $CDCl_3$, 125 MHz): δ 30.8, 34.0, 87.6, 120.5, 122.6, 137.4, 151.9, 172.9, 193.9, 203.6, 204.1, 207.0. IR (υ_{CO}, KBr, cm^{-1}): 1911 (s), 1913 (s), 1989 (s), 2071 (s).

Synthesis of 1d Complex **1d** was synthesized in the same way as described above for the synthesis of **1a** using $\mathbf{L}^4$H (0.280 g, 1.408 mmol) and $Ru_3(CO)_{12}$ (0.300 g, 0.469 mmol). Complex **1d**

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was obtained as brown orange crystals (yield 0.326 g, 76.3%). Anal. Calc. for $C_{34}H_{24}N_4O_{10}Ru_3$: C, 44.20; H, 2.62; N, 3.03. Found (%): C, 44.35; H, 2.80; N, 2.96; ^{1}H NMR (ppm in $CDCl_3$, 500 MHz): δ 1.99 (s, 6H, CH_3), 6.86 (d, J = 7.5 Hz, 4H, Ar-H), 7.19-7.24 (m, 6H, Ar-H), 7.38 (t, J = 6.0 Hz, 2H, Py-H), 7.49 (d, J = 8.0 Hz, 2H, Py-H), 7.81 (t, J = 7.5 Hz, 2H, Py-H), 8.84 (d, J = 4.5 Hz, 2H, Py-H). ^{13}C NMR (ppm in $CDCl_3$, 125 MHz): δ 55.2, 88.8, 113.7, 122.0, 123.6, 128.6, 135.8, 136.8, 150.8, 159.2, 169.1, 193.2, 202.5, 203.9, 206.1. IR (υ_{CO}, KBr, cm^{-1}): 1909 (s), 2020 (s), 2032 (s).

Synthesis of 1e Complex **1e** was synthesized in the same way as described above for the synthesis of **1a** using $\mathbf{L^5}$H (0.263 g, 1.408 mmol) and $Ru_3(CO)_{12}$ (0.300 g, 0.469 mmol). Complex **1e** was obtained as brown orange crystals (yield 0.316 g, 74.9%). Anal. Calc. for $C_{32}H_{20}N_2O_{10}Ru_3$: C, 42.91; H, 2.25; N, 3.13. Found (%): C, 42.73; H, 2.01; N, 3.37; ^{1}H NMR (ppm in $CDCl_3$, 500 MHz): δ 5.02 (s, 2H, CH), 6.71 (d, J = 7.5 Hz, 2H, Py-H), 7.02 (d, J = 7.5 Hz, 4H, Ar-H), 7.23-7.27 (m, 6H, Ar-H), 7.36 (t, J = 6.5 Hz, 2H, Py-H), 7.55 (t, J = 8.0 Hz, 2H, Py-H), 8.94 (d, J = 5.5 Hz, 2H, Py-H). ^{13}C NMR (ppm in $CDCl_3$, 125 MHz): δ 89.3, 122.1, 123.8, 127.4, 128.0, 128.5, 136.9, 143.3, 150.8, 168.9, 193.1, 202.5, 203.8, 206.1. IR (υ_{CO}, KBr, cm^{-1}): 1919 (s), 1988 (s), 2070 (s), 2017.07 (m).

Synthesis of 1f Complex **1f** was synthesized in the same way as described above for the synthesis of **1a** using $\mathbf{L^6}$H (0.312 g, 1.408 mmol) and $Ru_3(CO)_{12}$ (0.300 g, 0.469 mmol). Complex **1f** was obtained as brown orange crystals (yield 0.296 g, 68.3%). Anal. Calc. for $C_{34}H_{24}N_2O_{10}Ru_3$: C, 44.21; H, 2.62; N, 3.03. Found (%): C, 44.40; H, 2.49; N, 3.21; ^{1}H NMR (ppm in $CDCl_3$, 500 MHz): δ 3.75 (s, 6H, CH_3), 4.99 (s, 2H, CH), 6.67 (d, J = 8.0 Hz, 2H, Py-H), 6.77 (d, J = 9.0 Hz, 4H, Ar-H), 6.93 (d, J = 8.5 Hz, 4H, Ar-H), 7.34 (t, J = 6.5 Hz, 2H, Py-H), 7.53 (t, 2H, J = 7.5 Hz, Py-H), 8.92 (d, J = 5.5 Hz, 2H, Py-H). ^{13}C NMR (ppm in $CDCl_3$, 125 MHz): δ 55.2, 88.8, 113.7, 122.0, 123.6, 128.6, 135.8, 136.8, 150.8, 159.2, 169.1, 193.2, 202.5, 203.9, 206.1. IR (υ_{CO}, KBr, cm^{-1}): 1907 (m), 1975 (m), 1994 (m), 2070 (w).

Synthesis of 1g Complex **1g** was synthesized in the same way as described above for the synthesis of **1a** using $\mathbf{L^7}$H (0.304 g, 1.408 mmol) and $Ru_3(CO)_{12}$ (0.300 g, 0.469 mmol). Complex **1g** was obtained as brown orange crystals (yield 0.304 g, 67.7%). Anal. Calc. for $C_{34}H_{24}N_2O_{12}Ru_3$: C, 42.73; H, 2.53, N, 2.93. Found (%): C, 42.84; H. 2.38; N, 2.72; ^{1}H NMR (ppm in $CDCl_3$, 500 MHz): δ 3.78 (s, 6H, CH_3), 5.02 (s, 2H, CH), 6.70 (d, J = 8.0 Hz, 2H, Py-H), 6.81 (d, J = 8.5 Hz, 4H, Ar-H), 6.96 (d, J = 8.5 Hz, 4H, Ar-H), 7.36 (t, J = 6.5 Hz, 2H, Py-H), 7.56 (d, J = 6.5 Hz, 2H, Py-H), 8.94 (d, J = 5.0 Hz, 2H, Py-H). ^{13}C NMR (ppm in $CDCl_3$, 125 MHz): δ 55.2, 88.8, 113.7, 122.0, 123.6, 128.6, 135.8, 136.8, 150.8, 159.2, 169.1, 193.2, 202.5, 203.9, 206.1. IR (υ_{CO}, KBr, cm^{-1}): 1899 (s), 1938 (m), 2007 (s), 2026 (s).

Synthesis of 1h Complex **1h** was synthesized in the same way as described above for the synthesis of **1a** using $\mathbf{L^8}$H (0.309 g, 1.408 mmol) and $Ru_3(CO)_{12}$ (0.300 g, 0.469 mmol). Complex **1h** was obtained as brown orange crystals (yield 0.309 g, 68.9%). Anal. Calc. for $C_{32}H_{18}Cl_2N_2O_{10}Ru_3$: C, 39.84; H, 1.88; N, 2.90. Found (%): C, 39.66; H, 2.09; N, 2.72; ^{1}H NMR (ppm in $CDCl_3$, 500 MHz): δ 4.97 (s, 2H, CH), 6.68 (d, J = 7.5 Hz, 2H, Py-H), 6.95 (d, J = 8.5 Hz,. 4H, Ar-H), 7.23 (d, J = 8.5 Hz, 4H, Ar-H), 7.38 (t, J = 6.5 Hz, 2H, Py-H), 7.58 (t, J = 7.5 Hz, 2H, Py-H), 8.93 (d, J = 5.0 Hz, 2H, Py-H). ^{13}C NMR (ppm in $CDCl_3$, 125 MHz): δ 88.6, 122.0, 124.1, 128.6, 128.7, 133.8, 137.1, 141.8, 151.0, 168.3, 192.8, 202.5, 203.7, 205.9. IR (υ_{CO}, KBr, cm^{-1}): 1910 (w), 1997 (m), 2078 (w).

Synthesis of 1i Complex **1i** was synthesized in the same way as described above for the synthesis of **1a** using $\mathbf{L^9}$H (0.373 g, 1.408 mmol) and $Ru_3(CO)_{12}$ (0.300 g, 0.469 mmol). Complex **1i** was obtained as brown orange crystals (yield 0.384 g, 77.7%). Anal. Calc. for$C_{32}H_{18}Br_2N_2O_{10}Ru_3$: C, 36.48; H, 1.72; N, 2.66. Found (%): C, 36.59; H, 1.89; N, 2.42; ^{1}H NMR (ppm in $CDCl_3$, 500 MHz): δ 4.95 (s, 2H, CH), 6.68 (d, J = 8.0 Hz, 2H, Py-H), 6.89 (d, J = 8.0 Hz, 4H, Ar-H), 7.36 (m, 4H, Ar-H, 2H, Py-H), 7.57 (t, J = 7.5 Hz, 2H, Py-H), 8.92 (d, J = 5.5 Hz, 2H, Py-H). ^{13}C NMR (ppm in $CDCl_3$, 125 MHz): δ 88.7, 121.8, 122.0, 124.1, 128.9, 131.7, 137.1, 142.2, 151.0, 168.2, 192.7, 202.5, 203.7, 205.9. IR (υ_{CO}, KBr, cm^{-1}): 1906 (w), 1919 (s), 1987 (s), 2077 (s).

Synthesis of 1j Complex **1j** was synthesized in the same way as described above for the synthesis of **1a** using $\mathbf{L^{10}}$H (0.356 g, 1.408 mmol) and $Ru_3(CO)_{12}$ (0.300 g, 0.469 mmol). Complex **1j** was obtained as brown orange crystals (yield 0.305 g, 62.8%). Anal. Calc. for $C_{34}H_{18}F_6N_2O_{10}Ru_3$: C, 39.58; H, 1.76; N, 2.72. Found (%): C, 39.63; H, 1.91; N, 2.54; ^{1}H NMR (ppm in $CDCl_3$, 500 MHz): δ 5.03 (s, 2H, CH), 6.71 (d, J = 8.0 Hz, 2H, Py-H), 7.15 (d, J = 8.0 Hz, 4H, Ar-H), 7.42 (t, J = 6.5 Hz, 2H, Py-H), 7.52 (d, J = 8.0 Hz, 4H, Ar-H), 7.62 (t, J = 7.5 Hz, 2H, Py-H), 8.96 (d, J = 5.0 Hz, 2H, Py-H). ^{13}C NMR (ppm in $CDCl_3$, 125 MHz): δ 88.7, 122.0, 124.2, 125.6, 126.8, 127.5, 130.1, 137.3, 146.9, 151.1, 168.0, 192.5, 202.4, 203.5, 205.8. IR (υ_{CO}, KBr, cm^{-1}): 1915 (m), 1989 (s), 2070 (m).

Procedure for catalytic oxidation of alcohols To a solution of alcohol (1.0 mmol) in solvent (5.0 mL), the ruthenium complex (0.03 mmol) and TEMPO (0.1 mmol) was added, the mixture was refluxed under air atmosphere for requisite time. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was subject to purification by Al_2O_3 column chromatography (ethylacetate/hexane) to afford the corresponding product. Target product was identified by NMR and yield of ketone was determined by isolated yield.

X-ray Crystal Structural Determination

The crystals were mounted on a glass fiber using the oil drop. Data obtained with the ω-φscan mode were collected on a Bruker AXS SMART 1000 CCD diffractometer with graphite-monochromated Mo-K radiation (λ = 0.71073 Å). The structures were solved using direct methods, while further refinement with full-matrix least squares on F^2 was obtained with the SHELXTL program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

Conflicts of interest

There are no conflicts to declare.

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DOI: 10.1039/C8NJ00329G

Acknowledgements

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (No. 21372061), the Hebei Natural Science Foundation of China (No. B2017205006), and the Key Research Fund of Hebei Normal University (No. L2017Z02).

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DOI: 10.1039/C8NJ00329G

Table of Contents

Several new trinuclear ruthenium carbonyl complexes were synthesized and their application for aerobic oxidation of secondary alcohols was also established.