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FULL PAPER

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Synthesis of a series of new ruthenium organometallic complexes derived from pyridine-imine ligands and their catalytic activity in oxidation of secondary alcohols

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Reactions of pyridine imines [C_5H_4N-2-C(H) = N-C_6H_4-R] [R = H (1), CH_3 (2), OMe (3), CF_3 (4), Cl (5), Br (6)] with $Ru_3(CO)_{12}$ in refluxing toluene gave the corresponding dinuclear ruthenium carbonyl complexes of the type $\{\mu$-η^2-CH[(2-C_5H_4N)(N-C_6H_4-R)]$\}_2Ru_2(CO)_4(\mu$-CO) [R = H (7); CH_3 (8); OMe (9); CF_3 (10); Cl (11); Br (12)]. All six novel complexes were separated by chromatography, and fully characterized by elemental analysis, IR, NMR spectroscopy. Molecular structures of 7, 10, 11, and 12 were determined by X-ray crystal diffraction. Further, the catalytic performance of these complexes was also tested. The combination of $\{\mu$-η^2-CH[(2-C_5H_4N)(N-C_6H_4-R)]$\}_2Ru_2(CO)_4(\mu$-CO) and NMO afforded an efficient catalytic system for the oxidation of a variety secondary alcohols.

KEYWORDS
alcohol oxidation, pyridine-imine ligand, ruthenium complex, synthesis

1 | INTRODUCTION

Schiff bases are one of the most prevalent ancillary ligands in organometallic chemistry. These materials which have oxygen and nitrogen donor atoms operate as good chelating agents for transition metals.[1–4] Their metal complexes have a variety of biological, medicinal and analytical applications, in addition to their important roles in catalysis and organic syntheses.[5–12]

Synthesis of carbonyl compounds via alcohol oxidation is one of fundamental reactions in organic chemistry.[13] Alcohol oxidation reaction is widely investigated in both laboratories and industrial applications due to the importance of its valuable products such as aldehydes and ketones, which are widely used in dyestuff, polymer precursors, pharmaceutical and agrochemical industries.[14] Conventionally, most

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reactions require stoichiometric amounts oxidation reagents such as dichromate[15] or permanganate[16] used in the liquid phase. These oxidations are often toxic and harmful to the environment, removal of traces of these reagents from the reaction mixture is costly and difficult. In recent years, considerable efforts have been devoted to the development of alcohol oxidation.[17–23] For example, employing O_2 would be highly desirable to avoid toxic and hazardous stoichiometric oxidants. For this reason, several studies have focused on utilizing molecular oxygen as oxidant in aerobic oxidation reactions[24] But due to the poor oxidation performance of O_2 itself, the reaction time was more than 20 hr (even up to 48 hr) and the strong base and TEMPO were also needed as additives to achieve high conversion or yield. Therefore, the development of more efficient alcohol oxidation system is still an important research area.

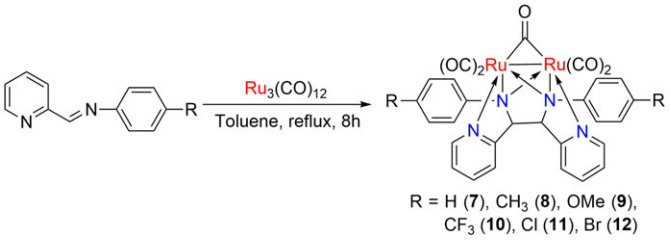
Alternatively, stable nitroxyl radicals, expecially N-methylmorpholine-N-oxide (NMO), have been used as oxidant for mild and selective oxidation of alcohols to aldehydes, ketones.[25] In 2011, karvembu and co-workers reported a series of Ru (II) complexes, [RuCl(L)(CO)$(PPh_3)_2$] {where L = *N*-[di (alkyl/aryl)carbamothioyl] benzamide derivatives}, which could oxidize a wide variety of alcohols to corresponding aldehydes or ketones in high yields in the presence of NMO.[26] Recently, Mondal et al. showed cis-(CO)-trans-(X)-[Ru $(CO)_2(HL)X_2$] (where X = Cl and I)-NMO to be an efficient catalytic system in alcohol oxidation.[27] Inspired by these studies and based our continuing efforts in creating novel ruthenium organometallic complexes, herein, we report the synthesis, characterization, and oxidation of secondary alcohols catalyzed by ruthenium pyridine-imine based complexes in the presence of N-methylmorpholine-N-oxide as oxidant.

2 | RESULTS AND DISCUSSION

2.1 | Reactions of pyridine-imine ligands $[C_5H_4N\text{-}2\text{-}C(H) = N\text{-}C_6H_4\text{-}R]$ [R = H (1); CH_3 (2); OMe (3); CF_3 (4); Cl (5); Br (6)] with $Ru_3(CO)_{12}$ in toluene

When pyridine-imines $[C_5H_4N\text{-}2\text{-}C(H) = N\text{-}C_6H_4\text{-}R]$ [R = H (**1**); CH_3 (**2**); OMe (**3**); CF_3 (**4**); Cl (**5**); Br (**6**)] were reacted with $Ru_3(CO)_{12}$ in refluxing toluene for 8 hr, the corresponding complexes $\{\mu\text{-}\eta^2\text{-}CH[(2\text{-}C_5H_4N)(N\text{-}C_6H_4\text{-}R)]\}_2Ru_2(CO)_4(\mu\text{-}CO)$ [R = H (**7**); CH_3 (**8**); OMe (**9**); CF_3 (**10**); Cl (**11**); Br (**12**)] were obtained in 40–77% yields (Scheme 1).

The IR spectra of **7~12** all exhibited two strong terminal carbonyl absorption at 2000 cm^{-1} and a bridging carbonyl absorption at 1900 cm^{-1}. The ^1H NMR spectra of the diruthenium complexes **7~12** are similar, and they all show four groups of peaks at 7.29~8.71 ppm for the pyridyl protons and two doublets at 6.38~7.38 ppm for phenyl protons, plus one singlet for the carbon bridge protons at 4.54~4.87 ppm. The molecular structures of **7**, **10**, **11** and **12** are presented in Figures 1–4, respectively with the selected bond lengths and angles in the captions. The crystallographic data of these compounds in CIF or other electronic format see Supporting Information. Complexes **7**, **10**, **11** and **12** are carbon bridged diruthenium complexes, in which the functional group C=N of two ligands simultaneously coupled to form a C-C bridged ligand. These complexes all contain a Ru $(CO)_2(\mu\text{-}CO)$ Ru $(CO)_2$ unit, coordinated with the ligand. The Ru(1) and Ru(2) are coordinated with two nitrogen atoms in the chain bridge, an intramolecular nitrogen atom of the pyridyl, two terminal CO and a bridging CO. Bridged ligands are simultaneously coordinated to two ruthenium atoms with a μ_2-N atom behaving as a three-electron donor. The Ru-Ru bond distances are 2.8558(11) Å for **7**, 2.8580(5) Å for **10**, 2.8676(5) Å for **11** and 2.8659(9) Å for **12**, respectively. Disorder on the location of CF_3 has been shown in Figure 2. These complexes are unexpected products and the structures are unusual. On the basis of our previous research results,[28,29] we believe that the reaction pathway may undergo a process of carbon radical generation and coupling. A proposed mechanism for the formation of these complexes is proposed in Scheme 2. First, the N atom on pyridine coordinates to the Ru atom forming N-Ru coordinate bond. Then the single electron of Ru atom and N atom of Schiff base generates N-Ru covalent bond. At the same time, the C=N double bond of Schiff base occurs homolytic reaction, formation of a single electron on C atom and N atom, while another ligand has the same reaction, the final coupling of C atom and C atom to form C-C covalent bond, while the two N atom with another Ru atom generates N-Ru coordination bond respectively.



SCHEME 1 Synthesis of the complexes **7–12**

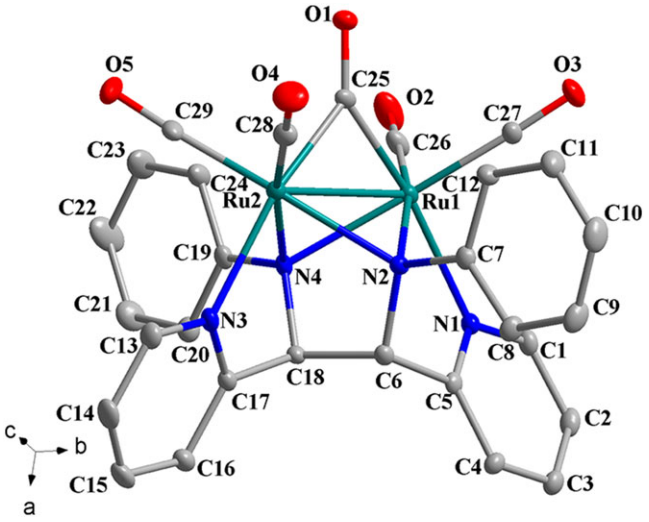


FIGURE 1 ORTEP view of cluster **7** showing 10% ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)-Ru(2) 2.8558(11), Ru(1)-N(1) 2.257(5), Ru(1)-N(2) 2.186(5), N(2)-Ru(1)-N(1) 77.95(18), N(4)-Ru(1)-N(1) 87.31(16), N(4)-Ru(1)-Ru(2) 49.26(12), Ru(1)-C(25)-Ru(2) 89.8(2), N(4)-Ru(2)-N(3) 77.3(2), N(2)-Ru(2)-N(3) 87.32(17)

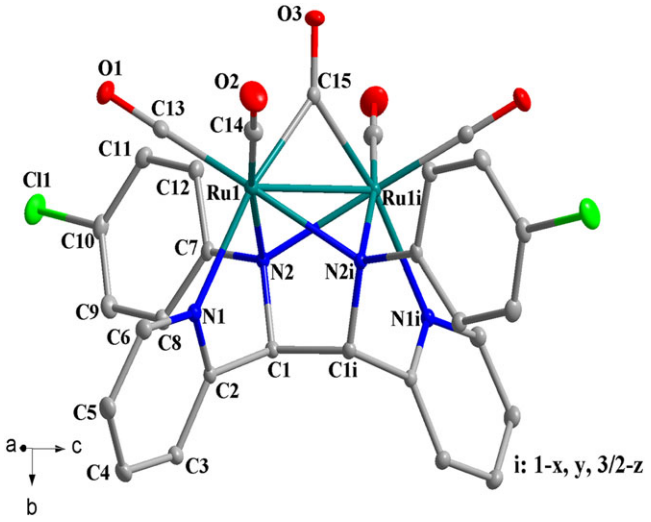


FIGURE 3 ORTEP view of cluster **11** showing 10% ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)-Ru(1i) 2.8676(5), Ru(1)-N(1) 2.248(3), Ru(1)-N(2) 2.171(3), Ru(1)-C(15) 2.032(4), N(2)-Ru(1)-N(1) 79.01(10), N(2i)-Ru(1)-N(1) 87.07(10), N(2)-Ru(1)-N(2i) 69.36(12), N(1)-Ru(1)-Ru(1i) 119.16(7), Ru(1i)-C(15)-Ru(1) 89.7(2)

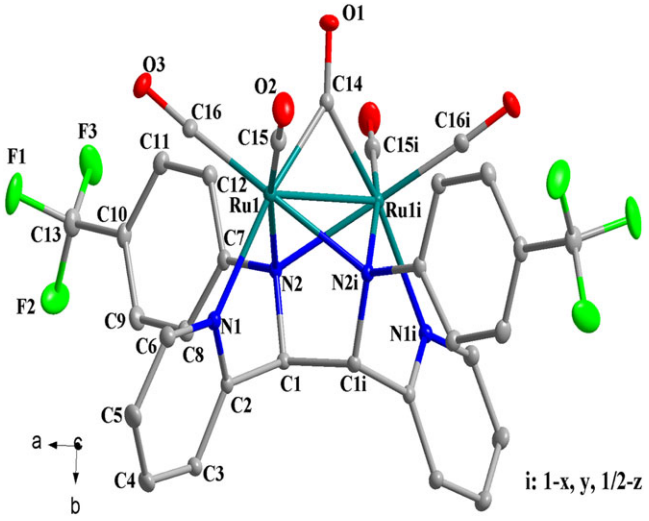


FIGURE 2 ORTEP view of cluster **10** showing 10% ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)-Ru(1i) 2.8580(5), Ru(1)-N(1) 2.260(3), Ru(1)-N(2) 2.181(2), Ru(1)-C(14) 2.026(3), N(2)-Ru(1)-N(1) 77.98(10), N(1)-Ru(1)-Ru(1i) 119.11(7), O(1)-C(14)-Ru(1) 135.14(10), Ru(1)-N(2)-Ru(1i) 80.67(8), Ru(1)-C(14)-Ru(i) 89.72(19)

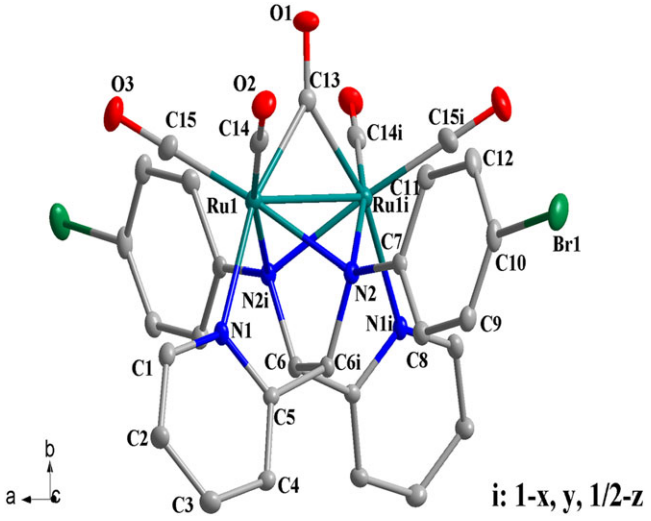
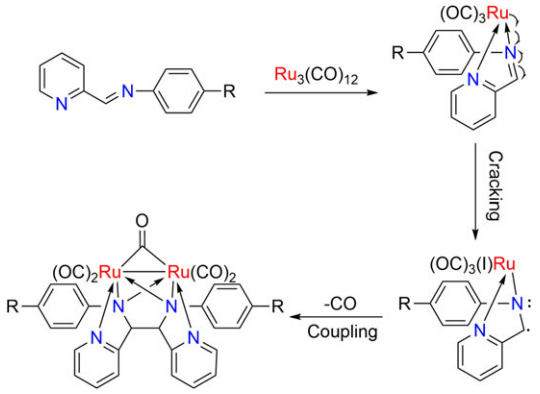


FIGURE 4 ORTEP view of cluster **12** showing 10% ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)-Ru(1i) 2.8659(9), Ru(1)-N(1) 2.245(5), Ru(1)-N(2) 2.165(5), Ru(1)-C(13) 2.049(8). N(2)-Ru(1)-N(1) 78.61(19), N(2i)-Ru(1)-N(1) 86.97(18), N(1)-Ru(1)-Ru(1i) 118.81(13), Ru(1)-N(2)-Ru(1i) 81.07(17), Ru(1i)-C(13)-Ru(1) 88.7(4)

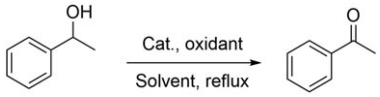
2.2 | Catalytic oxidation

To develop an optimal catalytic system, the oxidation of 1-phenylethanol was chosen as a model reaction (Scheme 3) and the results are summarized in Table 1. Our investigation began with complex **7** as a precatalyst under the condition that 1.0 mmol 1-phenylethanol was stirred with 3.0 mmol H_2O_2 in 6 mL CH_2Cl_2 at 40 °C under argon. As shown in Table 1, the reaction only gave the acetophenone product in 13% yield (entry 1). A search for more oxidants and solvents was pursued. Subsequently, TEMPO as co-oxidant has been examined, the desired product was obtained in 32% yield by simply replacing H_2O_2 with TEMPO (entry 2). Eventually, the



SCHEME 2 A plausible mechanism for the formation of **7–12**

targeted product with 81.0% yield was obtained when using CH_3CN as the solvent and NMO (3 mmol) as the oxidant (entry 12). Note that the reaction can proceed at a shorter time (1 hr) with complex **7** as a precatalyst, thus it is complementary to the conditions described in entry 14. The solvent screening indicated that CH_3CN was the most suitable solvent for the oxidation reaction. It can be concluded that complex **7** (0.01 mmol) as catalyst, in combination with 3 mmol NMO as oxidant in acetonitrile



SCHEME 3 The oxidation of 1-phenylethanol

are the optimal reaction conditions for the oxidation of aromatic alcohols.

Under the optimal reaction conditions, all six of ruthenium complexes proved to be capable of catalyzing oxidation of alcohols. A variety of secondary alcohols smoothly underwent the oxidation. The yields% was found to vary with the different catalysts, the catalytic results of complexes **7–12** are shown in Table 2. Generally, the present reactions were compatible with various groups, e.g. alkoxy, bromo, chloro and trifluoromethyl groups (Table 2, entries 2–5). The 1-phenylethanol with methoxy substituent was excellent substrate (Table 2, entry 2). When the 1-phenylethanols with electron withdrawing substituents were employed as the substrates, all the oxidation reactions proceeded smoothly with excellent yields (Table 2, entries 3–6). Cyclohexanol and 2-hexanol were all excellent substrates (Table 2, entries 7 and 8). The reaction of cyclohexanol gave the targeted product in 82–97% yield, while the reaction of 2-hexanol gave the targeted product in 85–98% yield. Aryl or alkyl secondary alcohols underwent this transformation to give the ketone products in good to excellent yields. Thus, the ruthenium complexes as catalyst could catalyze the oxidation of the secondary alcohols with high activities.

Based on our preliminary data and related Ru-catalyzed alcohol oxidation processes, a proposed mechanism for the present $\{\mu\text{-}\eta^2\text{-CH}[(2\text{-}C_5H_4N)(N\text{-}C_6H_4\text{-}R)]\}_2Ru_2(CO)_4(\mu\text{-CO})$/NMO-catalyzed alcohol oxidation was as shown in Scheme 4. First, the diruthenium

TABLE 1 Optimization of oxidation of 1-phenylethanol using **7**[a]

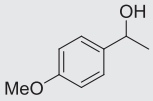
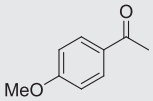
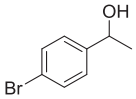
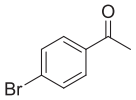
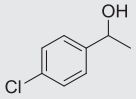
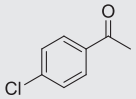
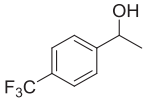
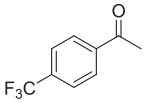
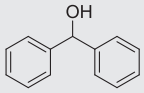
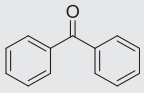
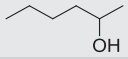
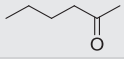
Entry	Cat.7 [mmol]	Oxidant	C:O ratio[b]	Temp [°C]	Solvent	Time [h]	Yield[c] [%]
1	0.01	H_2O_2	1:300	40	CH_2Cl_2	6	13
2	0.01	TEMPO	1:300	40	CH_2Cl_2	6	32
3	0.01	NMO	1:300	40	CH_2Cl_2	6	62
4	0.01	NMO	1:200	40	CH_2Cl_2	6	42
5	0.01	NMO	1:400	40	CH_2Cl_2	6	55
6	0.005	NMO	1:300	40	CH_2Cl_2	6	36
7	0.02	NMO	1:300	40	CH_2Cl_2	6	58
8	0.03	NMO	1:300	40	CH_2Cl_2	6	56
10	0.01	NMO	1:300	40	toluene	6	26
9	0.01	NMO	1:300	40	CH_3CN	6	70
11	0.01	NMO	1:300	60	CH_3CN	6	75
12	0.01	NMO	1:300	80	CH_3CN	6	81
13	0.01	NMO	1:300	80	CH_3CN	2	82
14	0.01	NMO	1:300	80	CH_3CN	1	81
15	0.01	NMO	1:300	80	CH_3CN	0.5	63

[a]Reaction conditions: 1.0 mmol 1-phenylethanol, 6 mL solvent.

[b]Catalyst: Oxidant ratio.

[c]Isolated yield was determined by column chromatography.

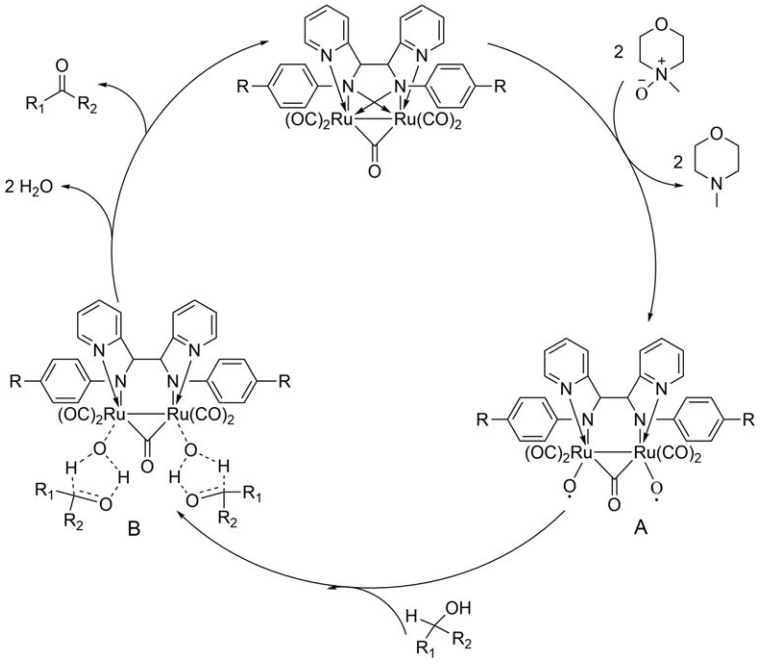
TABLE 2 Oxidation of various substrates catalyzed by **7-12**[a]

Entry	Substrate	Product	Yield (%)					
			7	**8**	**9**	**10**	**11**	**12**
1[b]			81	85	75	84	73	77
2[b]			92	95	94	94	90	93
3[b]			81	95	92	97	86	98
4[b]			89	98	96	96	91	95
5[b]			80	89	86	87	82	86
6[b]			81	93	93	84	91	95
7[c]			82	97	91	91	89	90
8[c]			85	94	92	96	98	96

[a]Reaction conditions:1 mmol substrate, 0.01 mmol catalyst, 3.0 mmol NMO, 6 mL acetonitrile, 80 °C, 1 hr.

[b]Yield was determined by column chromatography.

[c]Yield was determined by GC.



SCHEME 4 A proposed mechanism for secondary alcohol oxidation catalyzed by diruthenium carbonyl complexes/NMO system

TABLE 3 Crystal data and structure refinement parameters for **7**, **10**, **11**, and **12**

Complex	7	10	11	12
Empirical formula	$C_{29}H_{20}N_4O_5Ru_2{\cdot}0.5THF$	$C_{31}H_{18}F_6N_4O_5Ru_2{\cdot}3THF$	$C_{29}H_{18}Cl_2N_4O_5Ru_2$	$C_{29}H_{18}Br_2N_4O_5Ru_2$
Formula weight	742.68	1058.95	775.51	864.43
Temperature (K)	298(2)	298(2)	298(2)	298(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pna2(1)*	*C2/c*	*C2/c*	*C2/c*
a (Å)	19.068(7)	25.641(2)	20.4589(18)	20.5609(18)
b (Å)	14.112(5)	9.2062(9)	8.9525(8)	9.0240(9)
c (Å)	11.648(4)	19.3391(18)	17.4122(15)	17.4441(15)
α (°)	90	90	90	90
β (°)	90	105.126(2)	115.739(3)	114.482(3)
γ (°)	90	90	90	90
V (Å^3)	3134.2(19)	4407.0(7)	2872.8(4)	2945.6(5)
Z	4	4	4	4
F (000)	1480	2136	1528	1672
Dcalc (g/cm^3)	1.574	1.596	1.793	1.949
Crystal dimensions (mm)	0.18 × 0.13 × 0.10	0.45 × 0.43 × 0.40	0.31 × 0.15 × 0.10	0.17 × 0.12× 0.04
θ Range (°)	2.27–25.02	2.36–25.02	2.53–25.02	2.18–25.02
Reflections collected	18044	10592	6863	6876
Independent reflections	5241	3887	2535	2593
R_{int}	0.0395	0.0247	0.0232	0.0869
Parameters	406	336	191	191
Goodness of fit on F^2	1.060	1.138	1.048	0.939
R_1, wR_2 [$I > 2\sigma(I)$]	0.0353, 0.0755	0.0310, 0.0727	0.0253, 0.0567	0.0478, 0.0651
R_1, wR_2 (all data)	0.0472, 0.0802	0.0477, 0.0829	0.0467, 0.0671	0.0990, 0.0715
CCDC deposition no.	1478744	1463119	1478743	1478745

complex reacted with two molecules of NMO to form the Ru-O free radical species A, which then reacted with an alcohol to afford a five-membered ring transition state intermediate B. Subsequently, Ru-O bond, C-H and O-H bond of the alcohol in intermediate B was gradually broken to release two molecules of H_2O and the C=O bond gradually formed accompanied by the generation of carbonyl product. Finally, intermediate B is reconverted to diruthenium complex to complete entire cycle.

3 | CONCLUSION

In summary, a series of novel ruthenium carbonyl complexes have been synthesized by reaction of pyridine imines [C_5H_4N-2-C(H) = N-C_6H_4-R] [R = H (1), CH_3 (2), OMe (3), CF_3 (4), Cl (5), Br (6)] with $Ru_3(CO)_{12}$ in refluxing toluene. The results clearly show that these complexes are dinuclear rhenium clusters, in which each rhenium atom is coordinated by three nitrogen atoms and two terminal carbonyls and the two Ru atoms is linked by a bridging carbonyl. In addition, the catalytic performance of these dinuclear ruthenium carbonyl complexes has been tested. The combination of {μ-η^2-CH[(2-C_5H_4N)(N-C_6H_4-R)]}$_2Ru_2(CO)_4$(μ-CO) and NMO afforded an efficient catalytic system for oxidation of a variety of secondary alcohols, giving the corresponding ketones in good to excellent yields.

4 | EXPERIMENTAL

4.1 | General considerations

4.1.1 | Materials

Schlenk and vacuum line techniques were employed for all manipulations of air- and moisture-sensitive complexes. All solvents were distilled from appropriate drying agents under an atmosphere of nitrogen prior to use.

Ligand precursors [C_5H_4N-2-C(H) = N-C_6H_4-R] [R = H (**1**); CH_3 (**2**); OMe (**3**); CF_3 (**4**); Cl (**5**); Br (**6**)] were prepared according to the literature methods.[30–33]

4.1.2 | Equipment and analyses

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV III-500 instrument, while IR spectra were recorded as KBr disks on a Thermo Fisher is50 spectrometer. X-ray measurements were made on a Bruker AXS SMART 1000 CCD diffractometer with graphite monochromated Mo $K\alpha$ (λ = 0.71073 Å) radiation. Elemental analyses were performed on a Vario EL III analyzer.

4.2 | Syntheses of ruthenium complexes

4.2.1 | Synthesis of 7

A solution of ligand precursor **1** (0.171 g, 0.938 mmol) and $Ru_3(CO)_{12}$ (0.300 g, 0.469 mmol) in 30 ml of toluene was heated at reflux for 8 hr. The solvent was then removed in vacuo, and the residue was placed in an Al_2O_3 column. Elution with ethyl acetate/petroleum ether developed a yellow band, which afforded 0.172 g (77.6%) of **7** as red crystals. Mp: 140.3 °C. Anal. Calcd for $C_{29}H_{20}N_4O_5Ru_2$: C, 49.29; H, 2.85; N, 7.93, Found (%): C, 49.49; H, 2.99; N, 7.77. ^{1}H NMR (ppm in DMSO-d_6, 500 MHz): δ 4.54 (s, 2H, CH), 6.70 (s, 2H, Ph-H), 7.07 (t, 4H, J = 8.0 Hz, Ph-H), 7.16 (d, 4H, J = 7.5 Hz, Ph-H), 7.29 (d, 2H, J = 5.5 Hz, Py-H), 7.70 (d, 2H, J = 6.5 Hz, Py-H), 7.86 (t, 2H, J = 7.5 Hz, Py-H), 8.42 (d, 2H, J = 2.5 Hz, Py-H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 70.1, 119.7, 120.4, 123.6, 124.7, 128.7, 139.7, 152.7, 158.6, 162.0, 193.1. IR (υ_{CO}, KBr, cm^{-1}): 2034(s), 2001(s), 1946(s).

4.2.2 | Synthesis of 8

By using a procedure similar to that described above, ligand precursor **2** reacted with $Ru_3(CO)_{12}$ gave product **8** in 48.5% yield as red solid. Mp: 151.3 °C; Anal. Calcd for $C_{31}H_{24}N_4O_5Ru_2$: C, 50.68; H, 3.29; N, 7.63, Found (%): C, 50.50; H, 3.45; N, 7.82. ^{1}H NMR (ppm in DMSO-d_6, 500 MHz): δ 2.09 (s, 6H, CH_3), 4.80 (s, 2H, CH), 6.81 (d, 4H, J = 8.5 Hz, Ph-H), 7.10 (d, 4H, J = 8.5 Hz, Ph-H), 7.42–7.44 (m, 2H, Py-H), 8.02–8.06 (m, 2H, Py-H), 8.19 (d, 2H, J = 8.5 Hz, Py-H), 8.50 (d, 2H, J = 5.0 Hz, Py-H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 70.2, 119.6, 123.6, 124.6, 129.0, 129.1, 139.6, 152.7, 156.2, 162.3, 200.4. IR (υ_{CO}, KBr, cm^{-1}): 2030(s), 1998(s), 1940(s).

4.2.3 | Synthesis of 9

By using a procedure similar to that described above, ligand precursor **3** reacted with $Ru_3(CO)_{12}$ gave product **9** in 54.8% yield as red solid. Mp: 156.3 °C; Anal. Calcd for $C_{31}H_{24}N_4O_7Ru_2$: C, 48.56; H, 3.16; N, 7.31, Found (%): C, 48.31; H, 3.38; N, 7.53. ^{1}H NMR (ppm in DMSO-d_6, 500 MHz): δ 3.65 (s, 6H, OCH_3), 4.82 (s, 2H, CH), 6.66 (d, 4H, J = 9.0 Hz, Ph-H), 7.19 (d, 4H, J = 9.0 Hz, Ph-H), 7.50 (t, 2H, J = 7.0 Hz, Py-H), 8.08–8.12 (m, 2H, Py-H), 8.24 (d, 2H, J = 8.0 Hz, Py-H), 8.58 (d, 2H, J = 5.0 Hz, Py-H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 55.5, 70.6, 113.8, 120.4, 123.6, 124.6, 139.5, 151.9, 152.7, 153.2, 162.4. IR (υ_{CO}, KBr, cm^{-1}): 2030(s), 1996(s), 1963(s).

4.2.4 | Synthesis of 10

By using a procedure similar to that described above, ligand precursor **4** reacted with $Ru_3(CO)_{12}$ gave product **10** in 69.1% yield as red crystals. Mp: 163.2 °C; Anal. Calcd for $C_{31}H_{18}F_6N_4O_5Ru_2$: C, 44.19; H, 2.15; N, 6.65, Found (%): C, 44.39; H, 2.40; N, 6.42. ^{1}H NMR (ppm in $CDCl_3$, 500 MHz): δ 4.55 (s, 2H, CH), 7.18 (d, 4H, J = 8.5 Hz, Ph-H), 7.30 (d, 4H, J = 9.0 Hz, Ph-H), 7.35–7.37 (m, 2H, Py-H), 7.73 (d, 2H, J = 7.5 Hz, Py-H), 7.90–7.93 (m, 2H, Py-H), 8.44 (d, 2H, J = 5.0 Hz, Py-H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 67.5, 120.0, 123.8, 124.9, 126.1, 140.0, 153.1, 161.2, 162.3, 199.9, 200.4. IR (υ_{CO}, KBr, cm^{-1}): 2040(s), 2008(s), 1954(s).

4.2.5 | Synthesis of 11

By using a procedure similar to that described above, ligand precursor **5** reacted with $Ru_3(CO)_{12}$ gave product **11** in 43.3% yield as red crystals. Mp: 157.5 °C; Anal. Calcd for $C_{29}H_{18}Cl_2N_4O_5Ru_2$: C, 44.91; H, 2.34; N, 7.22, Found (%): C, 44.79; H, 2.16; N, 7.38. ^{1}H NMR (ppm in $CDCl_3$, 500 MHz): δ 4.65 (s, 2H, CH), 7.22 (d, 4H, J = 8.0 Hz, Ph-H), 7.38 (t, 4H, J = 8.5 Hz, Ph-H), 7.82 (t, 2H, J = 8.5 Hz, Py-H), 8.17 (d, 2H, J = 7.5 Hz, Py-H), 8.58 (s, 2H, Py-H), 8.71 (d, 2H, J = 4.5 Hz, Py-H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 70.0, 111.4, 121.9, 123.7, 124.8, 129.1, 131.3, 139.8, 152.9, 158.0, 161.5. IR (υ_{CO}, KBr, cm^{-1}): 2033(s), 2004(s), 1945(s).

4.2.6 | Synthesis of 12

By using a procedure similar to that described above, ligand precursor **6** reacted with $Ru_3(CO)_{12}$ gave product

12 in 44.4% yield as red crystals. Mp: 159.6 °C; Anal. Calcd for $C_{29}H_{18}Br_2N_4O_5Ru_2$: C, 40.29; H, 2.10; N, 6.48, Found (%): C, 40.49; H, 2.35; N, 6.67. ^{1}H NMR (ppm in DMSO-d_6, 500 MHz): δ 4.86 (s, 2H, CH), 7.08 (d, 4H, J = 9.0 Hz, Ph-H), 7.21 (d, 4H, J = 9.0 Hz, Ph-H), 7.47 (t, 2H, J = 6.5 Hz, Py-H), 8.08 (t, 2H, J = 8.0 Hz, Py-H), 8.20 (d, 2H, J = 7.5 Hz, Py-H), 8.56 (d, 2H, J = 5.0 Hz, Py-H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 70.0, 121.3, 123.6, 123.7, 128.4, 132.0, 139.8, 152.9, 157.6, 161.5, 200.6. IR (υ_{CO}, KBr, cm^{-1}): 2035 (s), 2006 (s), 1947 (s).

4.3 | Crystal structure determination

Crystals of complexes **7**, **10, 11**, and **12** suitable for X-ray diffraction were investigated with a Bruker AXS SMART 1000 CCD diffractometer, using graphite monochromated Mo $K\alpha$ radiation (φ/ω scan, λ = 0.71073 Å). Semiempirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined by full-matrix least-squares. All calculations were done using the SHELXL-97 program system. Crystallographic data and experimental details of the structure determinations are given in Table 3. The single-crystal X-ray determinations are illustrated in Figures 1–3, 2–4, 4. CCDC 1478744, 1463119, 1478743, 1478745 for **7**, **10**, **11**, and **12**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk of www: http://www.ccdc.cam.ac.uk.

4.4 | Catalytic oxidation of various substrates

The catalytic activity of the prepared ruthenium complexes for the oxidation of various substrates was tested in the presence of NMO (N-methylmorpholine-N-oxide) as oxidant. A typical reaction using these complexes as catalyst and NMO as oxidant at 1:300 molar ratio is described as follows. The catalytic reaction was carried out under the following conditions: 0.01 mmol ruthenium complex catalyst, 3 mmol of NMO and 1.0 mmol substrate were mixed in 6 mL of CH_3CN. The reaction was stirred at 80 °C for 1 hr under 1 atmosphere. Solvent was evaporated from the mother liquor under reduced pressure and the residue was purified by Al_2O_3 column chromatography. Elution with petroleum ether/ethyl acetate (1:10, V/V) gave the desired product. The target product was identified by NMR and the NMR data are available in the supporting information.

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SUPPORTING INFORMATION

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