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Ruthenium Carbonyl Complexes with Pyridine-Alkoxide Ligands: Synthesis, Characterization and Catalytic Application in Dehydrgenative Oxidation of Alcohols

Zhiqiang Hao,‡ Xinlong Yan,‡ Kang Liu, Xiaohui Yue, Zhangang Han and Jin Lin*

Several new trinuclear ruthenium carbonyl complexes chelated with 6-bromopyridine alcohol ligands, [6-bromopyC$(CH_2)_4$O]$Ru_3(CO)_9$ (**1a**), [6-bromopyC$(CH_2)_5$O]$Ru_3(CO)_9$ (**1b**), [6-bromopyC$(Me)_2$O]$Ru_3(CO)_9$ (**1c**) and [6-bromopyCMeC_6H_5O]$Ru_3(CO)_9$ (**1d**), were synthesized from the reaction of $Ru_3(CO)_{12}$ with 6-bromopyC$(CH_2)_4$OH ($\mathbf{L^1}$H), 6-bromopyC$(CH_2)_5$OH ($\mathbf{L^2}$H), 6-bromopyC$(Me)_2$OH ($\mathbf{L^3}$H) and 6-bromopyCMeC_6H_5OH ($\mathbf{L^4}$H) in refluxing THF, respectively. The free ligands $\mathbf{L^1}$H-$\mathbf{L^4}$H were synthesized by the nucleophilic reaction of lithium salt (generated from 2, 6-dibromopyridine and *n*-BuLi) with corresponding ketones. Further, these pyridine-based ligands were characterized by NMR spectroscopy and elemental analyses. All the four ruthenium carbonyl complexes were well characterized by NMR, IR, single-crystal X-ray crystallography, etc. Complexes **1a**-**1d** were found to exhibit high catalytic activities for dehydrogenative oxidation of secondary alcohols to give their corresponding products in good to excellent yields.

Introduction

Efficient oxidation of alcohols into their corresponding aldehydes or ketones is an important transformation due to its wide application in organic synthesis.[1-2] In the past few decades, much effort has been devoted to the development of alcohol oxidation.[3-5] By using stoichiometric oxidants such as chromium oxide[6] and manganese oxide[7] etc., a wide range of alcohols could be converted to the target products. However, excess amounts of oxidants with respect to substrates were often needed to achieve high activities and even these oxidants were toxic and harmful to environment. To address this issue, the employment of molecular oxygen[8] or hydrogen peroxide[9] as oxidant has been reported so far. Thus, the quest for effective catalytic systems for converting alcohols continues to be an active area of research.

Alternatively, dehydrogenative oxidation of alcohols accompanied by release of dihydrogen without using any oxidants would be superior from the environment-friendly perspective. This method is not only considered as an atom-economical approach to access carbonyl compounds but also can avoid using of stoichiometric oxidants. Indeed, considerable progress has been made to dehydrogenize oxidation of alcohols catalyzed by transition metal complexes.[10-11] For instance, Fujita and co-works reported a series of Cp*Ir complexes which can efficiently catalyze dehydrogenative oxidation of alcohols to give ketone or carboxylic acid derivatives in good yields.[12] However, iridium is the most expensive noble metal and the applications based on these complexes are limited in industrial scale. Therefore, it is necessary to replace iridium with the cheap noble metal, *viz.*, ruthenium[10c,13] or earth-abundant metals.[14] Recently, Milstein et al. reported a pincer Mn-catalyzed dehydrogenative oxidation of primary alcohols, giving the corresponding intermediate aldehydes with good selectivity, which could further react with an amine to form imine with the loss of water and hydrogen gas as the sole byproducts.[15] Such highly active homogeneous organometallic catalysts are strongly desired in the area of dehydrogenation catalysis.

Pyridine alcohol compounds are proved to be universal ligands because of their strong coordination ability and good stability. Transition metal complexes supported by these *N,O*-bidentate ligands have been documented as catalysts for diverse organic transformations.[16,17] During the ongoing investigation of transition metal carbonyl complexes, we reported a series of active ruthenium and rhenium carbonyl complexes bearing pyridine-alkoxide ligands as catalysts for oxidation of secondary alcohols in the presence of different nitroxyl radicals.[18] However, these catalytic systems required large quantities of additives, which were difficult to recovery and also had an adverse effect on environment. On the basis of these premises, it is worthy to develop a green method for oxidation alcohols catalyzed by pyridylalkanol-based catalysts under mild conditions. Herein, we disclosed the synthesis of well-defined ruthenium carbonyl complexes containing several

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†Electronic Supplementary Information (ESI) available: Includes X-ray crystallographic data and refinements for complexes **1a**-**1d** in CIF format and NMR spectra of the products. See DOI: 10.1039/x0xx00000x

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6-bromopyridine-alkoxide ligands. Their catalytic activities for dehydrogenative oxidation of secondary alcohols without using any oxidants was also presented.

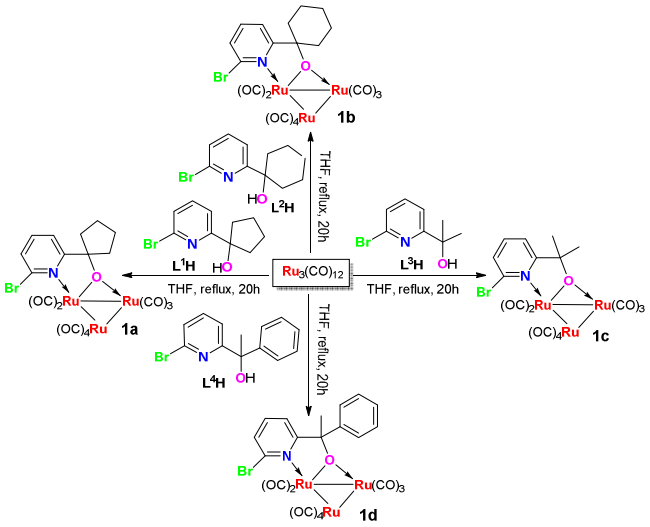
Results and discussion

Synthesis and characterization of 6-bromopyridine-alkoxide ligands

The ligand $\mathbf{L^3}$H was synthesized according to literature procedure and identified with NMR spectroscopy.[19] $\mathbf{L^1}$H-$\mathbf{L^2}$H and $\mathbf{L^4}$H were synthesized in a similar way. Lithiation of 2,6-dibromopyridine with *n*-BuLi was occurred firstly, then followed by addition of excess ketone. Subsequently, quenching the reaction with ammonium chloride aqueous solution resulted in the formation of 6-bromopyridine-alkoxide ligands in high yield. The ^{1}H NMR spectra of $\mathbf{L^1}$H-$\mathbf{L^2}$H and $\mathbf{L^4}$H showed the characteristic resonance at 3.68 ppm, 3.82 ppm and 4.96 ppm respectively assignable to the hydroxyl hydrogen protons.

Synthesis and characterization of ruthenium carbonyl complexes

Traditionally, transition-metal carbonyl complexes can be easily synthesized from treatment of transition-metal carbonyl clusters with organic ligands in refluxing solvent. Thus, the new trinuclear ruthenium carbonyl complexes were also synthesized with this strategy. Thermal treatment of $Ru_3(CO)_{12}$ with two equivalent pyridylalkanol ligands of 6-bromopyC$(CH_2)_4$OH ($\mathbf{L^1}$H), 6-bromopyC$(CH_2)_5$OH ($\mathbf{L^2}$H), 6-bromopyC$(Me)_2$OH ($\mathbf{L^3}$H) and 6-bromopyCMeC_6H_5OH ($\mathbf{L^4}$H) in refluxing THF were performed to give the corresponding triruthenium carbonyl complexes [6-bromopyC$(CH_2)_4$O]$Ru_3(CO)_9$ (**1a**), [6-bromopyC$(CH_2)_5$O]$Ru_3(CO)_9$ (**1b**), [6-bromopyC$(Me)_2$O]$Ru_3(CO)_9$ (**1c**) and [6-bromopyCMeC_6H_5O]$Ru_3(CO)_9$ (**1d**) in good yields, respectively (see scheme 1). All thesee new complexes were characterized by NMR spectroscopy, IR and single crystal X-ray diffraction analysis. In the ^{1}H NMR spectra of these complexes, the O*H* signals disappeared with respect to the one in free ligand, suggesting the deprotonation of ligands and coordination of hydroxyl groups to Ru atoms. In complex **1c**, the resonance of two methyl groups was split into two sharp singlet compared to free ligand $\mathbf{L^3}$H, demonstrating that the ligand was coordinated to ruthenium carbonyl clusters and two methyl groups were in different chemical environments. In IR spectra, all the complexes showed several strong absorption bands around 1925−2100 cm^{-1} due to the terminal carbonyls.



Scheme 1 Reactions of 6-bromo-substituted pyridine alcohols with $Ru_3(CO)_{12}$.

Crystal structures of complexes 1a-1d

The crystals that are suitable for X-ray structural determination were grown from a CH_2Cl_2/hexane mixed solvent system and the four ruthenium complexes were further confirmed by X-ray diffraction analysis. The crystallographic data of all these complexes were summarized in Table 1, indicating that crystals of complexes **1a** and **1c** belong to the monoclinic crystal system with $P2_1/n$ space group, **1b** is C_2/c space group.While complex **1d** crystallizes in triclinic system with P-1 space group. The molecular structures of **1a** and **1b** were shown in Figs. 1 and 2 together with selected bond distances and angles. In both of complexes, one molecular of ligand was coordinated to the $Ru_3(CO)_9$ unit in which three ruthenium atoms formed a close triangle. The Ru(1)-Ru(2) distances of 2.752(3) Å in **1a** and 2.754(8) Å in **1b** are significantly shorter than that found in those reported complexes of [μ-2-mesityl-(3-$Cy_2PC_9H_5$)](μ$_2$-CO)$Ru_3(CO)_9$ and [μ_2-η^1-2-(pyridin-2-yl)-3-$Cy_2PC_9H_6$]$Ru_3(CO)_9$[20][2.9390(7) Å and 2.9076(8) Å, respectively]. The Ru-O bonding distances (2.082 (2) Å for **1a**, 2.078 (5) Å for **1b**) are very similar to that of 2.076(4) Å in complex [Py$C(CH_2)_4]_2$[$Ru_3(CO)_8$].[18a] The molecular structures of **1c** and **1d** were shown in Figs. 3 and 4 with selected bond lengths and angels. The X-ray diffraction analysis reveals that **1c** and **1d** are also triruthenium complexes, which are similar to **1a** and **1b**. Three ruthenium atoms formed an approximately isosceles triangle with two shorter Ru-Ru distances in the range of 2.751(5)-2.763(7) Å and one long Ru-Ru distance [2.803 (5) Å for **1c** and 2.812 (7) Å for **1d**]. The bond distances of Ru-N are 2.239 (3) Å for **1c** and 2.228 (4) Å for **1d**, which are analogous to that in complexes **1a** and **1b** and also in agreement with that observed in $Ru_3(CO)_8(C_9H_6NO)$.[21] In complex **1d**, the dihedral angle between pyridine ring and phenyl ring is 87.1°, indicating that two six-membered rings are approximately paralleled to each other.

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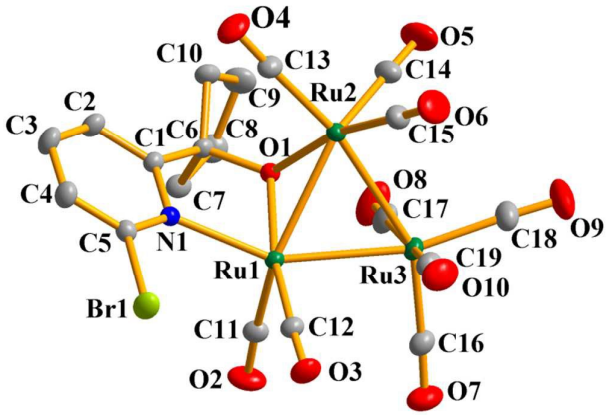

Fig. 1 Perspective view of **1a** with thermal ellipsoids are drawn at 30% probability level. Hydrogens have been omitted for clarity. The selected bond lengths (Å) and angles (°): Ru(1)-Ru(3) 2.7448(3), Ru(1)-Ru(2) 2.7524(3), Ru(2)-Ru(3) 2.8194(3), Ru(1)-N(1) 2.2219(19), Ru(1)-O(1) 2.0821(16), Ru(2)-O(1) 2.1283(17); Ru(1)-Ru(3)-Ru(2) 59.276(8), Ru(1)-O(1)-Ru(2) 81.64(6), O(1)-Ru(1)-Ru(2) 49.91(5), O(1)-Ru(2)-Ru(1) 48.45(4), N(1)-Ru(1)-Ru(3) 153.48(5), N(1)-Ru(1)-Ru(2) 92.26(5), O(1)-Ru(1)-N(1) 76.36(7).

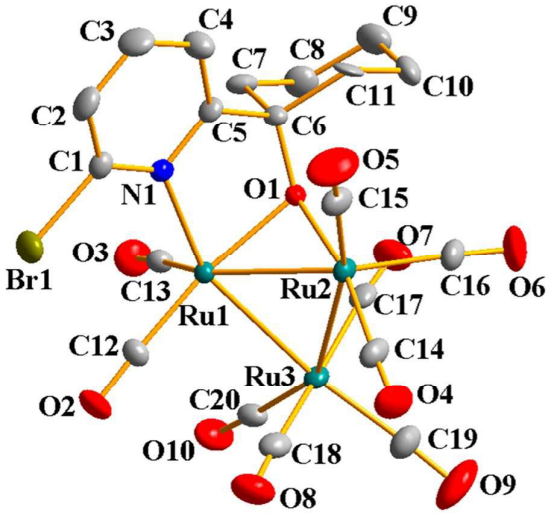

Fig. 2 Perspective view of **1b** with thermal ellipsoids are drawn at 30% probability level. Hydrogens have been omitted for clarity. The selected bond lengths (Å) and angles (°): Ru(1)-Ru(3) 2.7518(8), Ru(1)-Ru(2) 2.7549(8), Ru(3)-Ru(2) 2.8130(9), Ru(1)-O(1) 2.080(5), Ru(2)-O(1) 2.137(4), Ru(1)-N(1) 2.239(6); Ru(1)-Ru(3)-Ru(2) 59.33(2), Ru(1)-O(1)-Ru(2) 81.57(16), O(1)-Ru(1)-Ru(3) 83.37(13), O(1)-Ru(1)-Ru(2) 50.12(12), O(1)-Ru(2)-Ru(1) 48.31(12), O(1)-Ru(1)-N(1) 76.25(19), N(1)-Ru(1)-Ru(3) 153.09(14), N(1)-Ru(1)-Ru(2) 91.82(14).

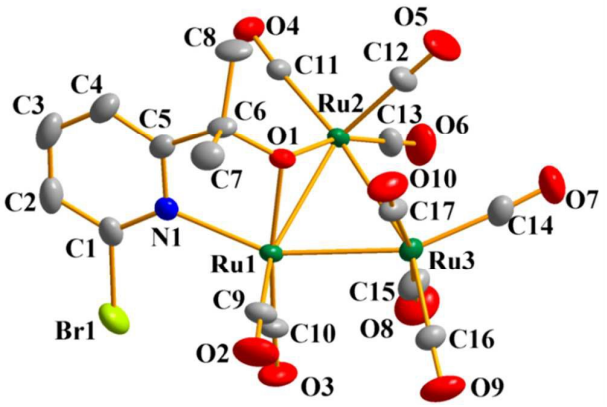

Fig. 3 Perspective view of **1c** with thermal ellipsoids are drawn at 30% probability level. Hydrogens have been omitted for clarity. The selected bond lengths (Å) and angles (°): Ru(1)-Ru(2) 2.7545(4), Ru(3)-Ru(1) 2.7517(5), Ru(3)-Ru(2) 2.8034(5), Ru(1)-N(1) 2.239(3), Ru(1)-O(1) 2.082(3), Ru(2)-O(1) 2.116(3); Ru(1)-Ru(3)-Ru(2) 59.443(11), Ru(1)-O(1)-Ru(2) 82.01(10), O(1)-Ru(1)-Ru(2) 49.52(7), O(1)-Ru(2)-Ru(1) 48.47(7), O(1)-Ru(1)-N(1) 76.30(12), N(1)-Ru(1)-Ru(2) 96.23(8), N(1)-Ru(1)-Ru(3) 155.63(9).

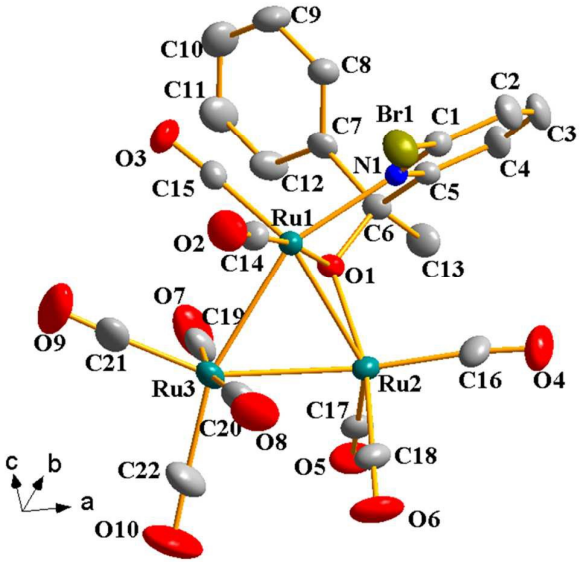

Fig. 4 Perspective view of **1d** with thermal ellipsoids are drawn at 30% probability level. Hydrogens have been omitted for clarity. The selected bond lengths (Å) and angles (°): Ru(1)-Ru(3) 2.7557(7), Ru(1)-Ru(2) 2.7630(7), Ru(2)-Ru(3) 2.8129(7), Ru(1)-N(1) 2.229(4), Ru(1)-O(1) 2.077(3), Ru(2)-O(1) 2.130(4); Ru(1)-Ru(3)-Ru(2) 59.484(17), Ru(1)-O(1)-Ru(2) 82.09(12), O(1)-Ru(1)-Ru(2) 49.77(10), O(1)-Ru(2)-Ru(1) 48.13(9), O(1)-Ru(1)-N(1) 76.57(15), N(1)-Ru(1)-Ru(3) 151.92(11), N(1)-Ru(1)-Ru(2) 90.67(11).

Table 1 Summary of the crystal data for compounds **1a-1d**.

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complex	1a	1b	1c	1d
Formula	$C_{19}H_{11}BrNO_{10}Ru_3$	$C_{20}H_{13}BrNO_{10}Ru_3$	$C_{17}H_9BrNO_{10}Ru_3$	$C_{22}H_{11}BrNO_{10}Ru_3$
F_w	796.41	810.43	770.37	832.44
Crystsyst	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$C2/c$	$P2_1/c$	P-1
a (Å)	16.7385(10)	16.1512(14)	8.9466(9)	9.3991(6)
b (Å)	10.0421(6)	10.1843(9)	17.8612(19)	10.5565(8)
c (Å)	15.8393(10)	30.492(3)	14.6199(16)	14.6602(11)
α (°)	90	90	90	84.592(2)
β (°)	116.3690(10)	91.1030(10)	96.403(2)	87.086(2)
γ (°)	90	90	90	70.2140(10)
V (Å^3)	2385.4(3)	5014.6(7)	2321.6(4)	1362.36(17)
Z	4	8	4	2
D_{calc}(mg/m^3)	2.218	2.147	2.204	2.029
μ (mm^{-1})	3.604	3.43	3.698	3.16
F(000)	1516	3096	1460	794
θ_{max} (°)	28.33	25.02	28.39	25.01
collected reflns	33491	12163	32584	6674
Uniq reflns	5897	4423	5765	4680
$R_{(int)}$	0.03	0.0529	0.0346	0.0183
GOF	0.991	1.157	1.022	1.072
R_1	0.0267	0.0472	0.041	0.0365
wR_2	0.0728	0.1015	0.1176	0.0706
Largest diff peak, hole (e Å^{-3})	0.845 and-1.198	0.681 and-1.196	0.868 and -1.635	1.181 and-0.648

Dehydrogenative oxidation of secondary alcohols

The catalytic performance of novel ruthenium carbonyl complexes were explored toward the dehydrogenative oxidation of secondary alcohols. In order to obtain the most appropriate conditions, we set out to evaluate various experiments using complex **1c** as catalyst and 1-phenylethanol as simple model substrate. The results were summarized in Table 2. First, the effect of base on this oxidative transformation was examined (Table 2, entries 1-4). When the reaction was performed using inorganic base, viz., Cs_2CO_3 and NaOH, only 48% and 12% yields of the product were obtained after 10 h under reflux (entries 1 and 2). While the employment of organic base, such as DABCO and DBU, the yields of desired product improved to 62% and 79%, respectively (entries 3 and 4). This phenomenon can be attributed to the poor solubility of inorganic salts in toluene. Analysis of the gas phase by GC revealed the formation of H_2. Subsequently, the loading of catalyst was screened. With the increase of **1c** loading from 0.5 to 2.0 mol % (compared to substrate), the yields of acetophenone were gradually enhanced from 79% to 97% (entries 4-6). Further the increase in amount of **1c** to 3.0 mol % lead to a relatively lower yield of 90%. Notable, the catalyst activity is strongly solvent-dependent. As shown in Table 2, use of polar solvent such as THF or CH_3CN had an adverse effect and only <60% of acetophenone was formed, with the rest being starting alcohol

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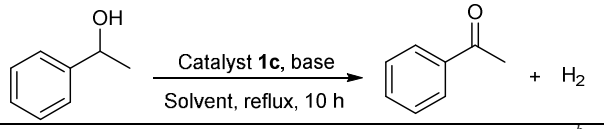
(entries 9 and 10). Then, switching to less polar solvent, i.e., xylene, the product was furnished in 77% yield. This is perhaps due the deactivation of the complex **1c** in high boiling point solvent. Increasing the amount of DBU from 0.2 to 0.4 mmol or 0.6 mmol resulted in 80%, 97% and 95% yields of acetophenone, respectively (entries 6, 11 and 12). Thus, 0.4 mmol of DBU was selected as the best amount of base. Finally, the control experiments showed that only trace amount of desired product was obtained in the absence of complex **1c** and a drastic decrease in yield was observed in the base-free condition (entries 13 and 14).

Table 2 Dehydrogenative oxidation of 1-phenylethanol catalyzed by complex **1c**[a]

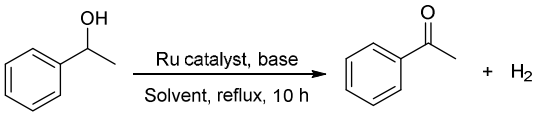


Entry	Cat.(mol%)	Base	Solvent	Yield (%)[b]
1	0.5	CS_2CO_3	toluene	48 (40)
2	0.5	NaOH	toluene	12
3	0.5	DABCO	toluene	62 (58)
4	0.5	DBU	toluene	79 (76)
5	1.0	DBU	toluene	84 (79)
6	2.0	DBU	toluene	97 (94)
7	3.0	DBU	toluene	88 (82)
8	2.0	DBU	xylene	77 (71)
9	2.0	DBU	THF	59 (55)
10	2.0	DBU	CH_3CN	51 (43)
11[c]	2.0	DBU	toluene	80 (77)
12[d]	2.0	DBU	toluene	95 (93)
13[e]	—	DBU	toluene	12
14[f]	2.0	—	toluene	35

[a] Reaction conditions: 1-phenylethanol (1.0 mmol), base (0.4 mmol), solvent (2.0 mL), 0.1MPa N_2, [b] Determined by GC analysis, isolated yields are indicated in parentheses. [c] Base (0.2 mmol). [d] Base (0.6 mmol). [e] without use of **1c**. [f] DBU was omitted.

We next examined the catalytic activity of complexes **1a-1d** having different sterically hindered substituents. Gratifyingly, complexes **1a** and **1b** in which cyclopentyl and cyclohexyl were at 2-position of pyridine respectively, were found to exhibit excellent catalytic performance for dehydrgenative oxidation of 1-phenylethanol to give the desired product in >90% yields (Table 3, entries 1 and 2). While the complex **1d** bearing both phenyl and methyl groups displayed relatively low activity, giving the acetophenone in 75% yield. Among complexes, the complex **1c** bearing the less sterically hindered substituent–two methyl groups–showed highest activity, producing 97% yield of acetophenone. Besides, the $Ru_3(CO)_{12}$ was also tested as catalyst for dehydrgenative oxidation of 1-phenylethanol and only 46% yield of acetophenone was obtained. Therefore, the optimized reaction condition was screened: alcohol (1.0 mmol), catalyst **1c** (2.0 mol%) and DBU (0.4 mmol) under refluxing toluene (2.0 mL) for 10h.

Table 3 Dehydrogenative oxidation of 1-phenylethanol catalyzed by complexes **1a-1d**[a]

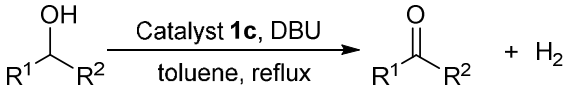


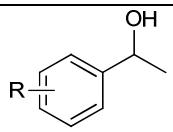
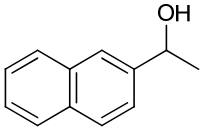
Entry	Catalyst	Base	Solvent	Yield (%)[b]
1	1a	DBU	toluene	96 (91)
2	1b	DBU	toluene	91 (88)
3[c]	1c	DBU	toluene	97 (94)
4	1d	DBU	toluene	88 (81)
5	$Ru_3(CO)_{12}$	DBU	toluene	46 (34)

[a] Reaction conditions: 1-phenylethanol (1.0 mmol), catalyst (2.0 mol%), DBU (0.4 mmol), toluene (2.0 mL), 0.1MPa N_2, [b] Determined by GC analysis, isolated yields are indicated in parentheses. [c] Entry 6 in Table 2.

With optimized conditions in hand, we then investigated the substrate scope. As shown in Table 4, various functional groups such as -Cl, -Br, -OMe, etc. were tolerated in this catalytic system. The substrates including substitutions at 3- and 4-positions of 1-phenylethanol underwent dehydrogentive oxidation effectively to form the corrsponding ketones in excellent yields (Table 4, entries 1-6). The reactions of sterically hindered 2-naphthylmethanol and diphenylmethanol were also dehydrogenated smoothly to give the desired products in > 90% yields (Table 4, entries 7 and 8). While aliphatic secondary cyclic and linear alcohols were reacted to give the corresponding ketones in moderate yields under same condition after 10h. Further extending the reaction time could increase yields to some extent (Table 4, entries 9-11).

Table 4. Dehydrogenative oxidation of secondary alcohols to ketones catalyzed by complexes **1c**[a]



Entry	Substrate	Time (h)	yield (%)[b]
			
1	R=*p*-CH_3	10	93 (88)
2	R=*p*-OCH_3	10	99 (95)
3	R=*p*-Cl	10	89 (81)
4	R=*p*-CF_3	10	93 (90)
5	R=*p*-Br	10	97 (88)
6	R=*m*-Br	10	90 (82)
7		10	96 (90)

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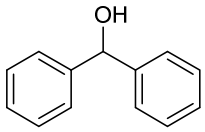
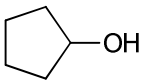
8		10	91 (83)
9		10	40
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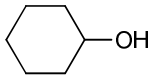
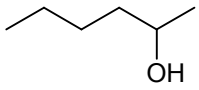
10		10	37
		20	58
11		10	57
		20	86

[a] Reaction conditions: alcohol (1.0 mmol), catalyst **1c** (2.0 mol%), DBU (0.4 mmol), solvent (2.0 mL), 0.1MPa N_2, [b] Determined by GC analysis, isolated yields are indicated in parentheses.

Conclusions

In conclusion, a series of new ruthenium carbonyl complexes with chelated 6-bromopyridylalkanol ligands had been synthesized. The free ligands $\mathbf{L^1}$H-$\mathbf{L^4}$H were synthesized by nucleophilic reaction of 6-bormopyridine lithium formed in situ with corresponding ketones. All the four ruthenium complexes were fully characterized by NMR, IR etc. The X-ray diffraction analysis revealed that complexes **1a-1d** were trinuclear ruthenium clusters, in which three Ru atoms formed an approximate isosceles triangle. The title ruthenium carbonyl complexes exhibited high efficiency and good functional group compatibility toward the dehydrogenative oxidation of secondary alcohols to form the target products in good to excellent yields, avoiding use of stoichiometric amounts of oxidants.

Experimental section

General considerations

All manipulations involving air- and/or moisture-sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. Toluene, xylene, diethyl ether, THF, and *n*-hexane were distilled under nitrogen in the presence of sodium and benzophenone. CH_2Cl_2 and CH_3CN were purified by distilling over calcium hydride before use. 2,6-dibromopyridine and *n*-BuLi were purchased from Sigma Aldrich. All the other chemical regents were also purchased from commercial sources and used as received unless otherwise indicated. ^{1}H and ^{13}C NMR spectra were measured using a Bruker Avance III-500 NMR spectrometer at room temperature with $CDCl_3$ as solvent. 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. Ligand $\mathbf{L^3}$H and other new ligands $\mathbf{L^1}$H, $\mathbf{L^2}$H and $\mathbf{L^4}$H were synthesized according to the literature procedure.[19]

Syntheses of the ligands and complexes

6-bromopyC$(CH_2)_4$OH ($\mathbf{L^1}$H) A hexane solution of *n*-BuLi (1.6 M, 9.5 mL, 15 mmol) was added dropwise at -78 °C over 15 min to an Et_2O (30 mL) solution of 2, 6-dibromopyridine (3.55 g, 15 mmol). The resulting dark red suspension was stirred at -78 °C for 1 h, followed by the addition of cyclopentanone (1.26 g, 15 mmol). The mixture was stirred at -78 °C for another 3 h, warmed to ambient temperature and continuously stirred overnight to obtain an orange solution. The saturated NH_4Cl solution (30 mL) was then added to the solution and extracted with CH_2Cl_2 (3 ×10 mL). The combined organic phases were dried with anhydrous $MgSO_4$ for several hours. Solvent was then removed under reduced pressure and the residue was placed in an Al_2O_3 column with ethyl acetate /petroleum ether as eluent to give $\mathbf{L^1}$H as yellow oil product (1.57 g, 43%). Anal. Calc. for $C_{10}H_{12}BrNO$: C, 49.61; H, 5.00; N, 5.79. Found (%): C, 49.76; H, 4.82; N, 5.60; ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.53 (t, *J* = 7.5 Hz, 1H, Py-*H*), 7.38 (d, *J* = 8Hz, 1H, Py-*H*), 7.34 (d, *J* = 7.5 Hz, Py-*H*), 3.69 (s, 1H, O*H*), 2.07-1.96 (m, 4H, cyclopentyl-CH_2), 1.95-1.89 (m, 2H, cyclopentyl-CH_2), 1.87-1.79 (m, 2H, cyclopentyl-CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 167.1, 140.5, 139.1, 126.0, 117.9, 83.1, 42.4, 24.6 ppm.

6-bromopyC$(CH_2)_5$OH ($\mathbf{L^2}$H) Compound $\mathbf{L^2}$H was synthesized in the same manner as for $\mathbf{L^1}$H with cyclohexanone (1.47 g, 15 mmol) as starting material. The pure product (1.31 g, 35%) was obtained as a yellow oil substance. Anal. Calc. for $C_{11}H_{14}BrNO$: C, 51.58; H, 5.51; N, 5.47. Found (%): C, 51.40; H, 5.64; N, 5.36; ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.54 (t, *J* = 7.5 Hz, 1H, Py-*H*), 7.37 (d, *J* = 8.0 Hz, 1H, Py-*H*), 7.35 (d, *J*= 7.5Hz, 1H, Py-*H*), 3.78 (s, 1H, O*H*), 1.79-1.77 (m, 4H, cyclohexyl-CH_2), 1.69-1.67 (m, 6H, cyclohexyl-CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 168.3, 140.6, 139.2, 126.1, 117.7, 73.1, 38.0, 25.4, 21.9 ppm.

6-bromopyCMeC$_6$H$_5$OH ($\mathbf{L^4}$H) Compound $\mathbf{L^4}$H was synthesized in the same manner as for $\mathbf{L^1}$H with acetophenone (1.81 g, 15 mmol) as starting material. The pure product (3.52 g, 85%) was obtained as a yellow oil substance. Anal. Calc. for $C_{13}H_{12}BrNO$: C, 56.14; H, 4.35; N, 5.04. Found (%): C, 56.28; H, 4.22; N, 5.17; ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.48-7.45 (m, 3H, Py-*H*, Ar-*H*), 7.36-7.29 (m, 3H, Py-*H*, Ar-*H*), 7.24 (t, *J* = 7.5 Hz, 2H, Py-*H*, Ar-*H*), 4.96 (s, 1H, O*H*), 1.91 (s, 3H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 166.7, 146.2, 140.4, 139.3, 128.3, 127.3, 126.5, 125.9, 119.1, 75.7, 29.4 ppm.

Complex 1a. A solution of $\mathbf{L^1}$H (0.23 g, 0.94 mmol) and $Ru_3(CO)_{12}$ (0.30 g, 0.47 mmol) in 30 mL of THF was heated at reflux for 24 h. After the mixture was cooled to ambient temperature, solvent was removed under reduced pressure. The residue was chromatographed on an Al_2O_3 column with ethyl acetate/petroleum ether as eluent to give **1a** as orange crystals (0.27 g, 73%). Anal. Calc. for $C_{19}H_{11}BrNO_{10}Ru_3$: C, 28.65; H, 1.39; N, 1.76. Found (%): C, 28.77; H, 1.55; N, 1.58; ^{1}H NMR (500 MHz, $CDCl_3$, 298 K):δ 7.58 (d, *J* = 7.8 Hz, 1H, Py-*H*), 7.53 (s, *J* = 10 Hz, 1H, Py-*H*), 7.20 (d, *J* = 7.7 Hz, 1H, Py-*H*), 2.33-2.24 (m, 2H, cyclopentyl-CH_2), 2.14-2.02 (m, 2H,

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cyclopentyl-CH_2), 1.97-1.83 (m, 2H, cyclopentyl-CH_2), 1.72-1.56 (m, 2H, cyclopentyl-CH_2) ppm. ^{13}C NMR(125 MHz, $CDCl_3$, 298 K):δ 206.4, 204.0, 203.1, 199.4, 197.1, 196.9, 193.2, 189.9, 185.2, 169.7, 146.7, 138.8, 128.6, 118.3, 101.8, 46.2, 44.6, 25.2, 24.4 ppm. IR(υ_{CO}, KBr, cm^{-1}): 2093 (s), 2059 (s), 2023 (s), 1998 (s), 1975 (s), 1929 (s).

Complex 1b. Complex **1b** was synthesized following analogous methods as described above for the synthesis of complex **1a** with the free ligand **L^2**H (0.24 g, 0.94 mmol) and $Ru_3(CO)_{12}$ (0.30 g, 0.47 mmol) as starting materials. Complex **1b** was obtained as orange crystals (0.29 g, 75%). Anal. Calc. for $C_{20}H_{13}BrNO_{10}Ru_3$: C, 29.64; H, 1.62; N, 1.73. Found (%): C, 29.51; H, 1.49; N, 1.84. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K):δ 7.57-7.51 (m, 2H, Py-*H*), 7.23 (d, *J* = 7.3 Hz, 1H, Py-*H*), 1.99-1.88(m, 4H, cyclohexyl-CH_2), 1.78-1.76 (m, 2H, cyclohexyl-CH_2), 1.55-1.52 (m, 2H, cyclohexyl-CH_2), 1.33-1.25 (m, 2H, cyclohexyl-CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K):δ 206.0, 204.3, 202.8, 199.3, 197.2, 196.6, 193.0, 189.5, 185.7, 170.7, 147.2, 138.8, 128.6, 118.8, 91.3, 43.8, 38.5, 25.4, 21.6, 20.7 ppm. IR(υ_{CO}, KBr, cm^{-1}): 1919 (s), 2023 (s), 2055 (s), 2096 (s).

Complex 1c. Complex **1c** was synthesized following analogous methods as described above for the synthesis of complex **1a** with the free ligand **L^3**H (0.20 g, 0.94 mmol) and $Ru_3(CO)_{12}$ (0.30 g, 0.47 mmol) as starting materials. Complex **1c** was obtained as orange crystals (0.30 g, 82%). Anal. Calc. for $C_{17}H_9BrNO_{10}Ru_3$: C, 26.50; H, 1.18; N, 1.82. Found (%): C, 26.39; H, 1.32; N, 1.68; ^{1}H NMR (500 MHz, $CDCl_3$, 298 K):δ 7.58 (d, *J* = 7.0 Hz, 1H, Py-*H*), 7.54 (t, *J* = 7.7 Hz, 1H, Py-*H*), 7.18 (d, *J* = 6.7 Hz, 1H, Py-*H*), 1.71 (s, 3H, CH_3), 1.58 (s, 3H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K):δ 206.6, 203.8, 203.0, 199.3, 196.7, 193.0, 189.9, 185.4, 170.1, 147.0, 138.9, 128.7, 118.8, 89.3, 34.3, 32.0 ppm. IR (υ_{CO}, KBr, cm^{-1}): 2095 (s), 2055 (s), 2026 (s), 2013 (s), 2001 (s), 1989 (s), 1965 (s), 1925 (s).

Complex 1d. Complex **1d** was synthesized following analogous methods as described above for the synthesis of complex **1a** with the free ligand **L^4**H (0.26 g, 0.94 mmol) and $Ru_3(CO)_{12}$ (0.30 g, 0.47 mmol) as starting materials. Complex **1d** was obtained as orange crystals (0.31 g, 78%). Anal. Calc. for $C_{22}H_{11}BrNO_{10}Ru_3$: C, 31.74; H, 1.33; N, 1.68. Found (%): C, 31.82; H, 1.46; N,1.52. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K):δ 7.89 (t, *J* = 7.7 Hz, 1H, Py-*H*), 7.51 (d, *J* = 7.8 Hz, 1 H, Py-*H*), 7.39 (t, *J* =5 Hz, 1H, Ar-*H*), 7.21-7.24 (m, 3H, Ar-*H*, Py-*H*), 6.87 (d, *J* = 6.3 Hz, 2H, Ar-*H*), 2.00 (s, 3H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K):δ 206.5, 206.0, 204.2, 196.2, 194.5, 191.0, 165.1, 152.8, 148.1, 137.5, 128.1, 128.0, 126.0, 124.2, 123.6, 93.5, 32.1 ppm. IR(υ_{CO}, KBr, cm^{-1}): 2093 (s), 2057 (s), 1964 (s), 1929 (s).

Procedure for dehydrgenative oxidation of secondary alcohols. A mixture of an alcohol substrate (1.0 mmol), complex **1c** (0.02 mmol) and DBU (0.4 mmol) in 2.0 mL of toluene was heated to refluxing temperature for 10 h under N_2 atmosphere. After required reaction period, the mixture was cooled to room temperature and the formed H_2 was vented off. The reaction products were analyzed by GC. Pure ketone derivatives were isolated by column chromatography using Al_2O_3 and further identified by comparison with authentic sample through NMR.

X-ray Crystal Structural Determination. Single crystals of complexes **1a-1d** (CCDC 1838366, 1576322, 1838365, 1573451) suitable for X-ray diffraction were obtained by crystallization from *n*-hexane/CH_2Cl_2 (1 : 3). Data obtained with the ω-2θ scan mode were collected on a Bruker AXS SMART 1000 CCD or SMART APEX II CCD diffractometer with graphite-monochromated Mo-K radiation (λ = 0.71073 A). The structures were refined on F^2 by full-matrix least-squares methods using the SHELXTL-97 program package. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced into calculated positions with the displacement factors of the host carbon atoms.

Conflicts of interest

There are no conflicts to declare.

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Dehydrgenative oxidation of secondary alcohols catalyzed by several new trinuclear ruthenium carbonyl complexes under mild conditions was displayed.