Received: 16 April 2021 | Revised: 3 June 2021 | Accepted: 4 June 2021

DOI: 10.1002/aoc.6336

RESEARCH ARTICLE

Applied Organometallic Chemistry WILEY

Preparation of trinuclear ruthenium clusters based on piconol ligands and their application in Oppenauer-type oxidation of secondary alcohols

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Funding information
Science Foundation of Hebei Normal University, Grant/Award Numbers: L2017Z02, L2018B08; Education Department Foundation of Hebei Province, Grant/Award Numbers: QN2019036, ZD2018005; Hebei Natural Science Foundation of China, Grant/Award Numbers: B2017205006, B2019205087

Abstract

Treatment of $Ru_3(CO)_{12}$ with one equivalent of 2-indolyl-6-pyridinyl-alcohol ligands 2-(C_8H_6N)-6-(CR^1R^2OH)C_5H_3N ($R^1 = R^2 = Me$ (**L1H**); $R^1 = R^2 = C_2H_5$ (**L2H**); R^1, $R^2 = -(CH_2)_4-$ (**L3H**);& R^1, $R^2 = -(CH_2)_5-$ (**L4H**)) in refluxing THF afforded the corresponding trinuclear ruthenium clusters L(μ_2-H)$Ru_3(CO)_9$ (**1a–1d**), respectively. All the novel Ru complexes were well characterized by NMR, elemental analyses and IR spectra. Structures of complexes **1a**, **1c**, and **1d** were further determined by X-ray crystallographic studies. Complexes **1a–1d** were applied to catalytic Oppenauer-type oxidation of secondary alcohols with acetone as oxidant, and complex **1a** was found to be the most efficient catalyst.

KEYWORDS

Oppenauer-type oxidation, piconol ligands, ruthenium clusters

1 | INTRODUCTION

Aldehydes and ketones are important intermediates that are widely used in pharmaceutical, polymer, and fine chemical industries.[1,2] The oxidation of alcohols to the corresponding carbonyl compounds is a fundamental reaction in organic synthesis.[3–5] Typical alcohol oxidation methods usually involve stoichiometric amounts of chromium-, manganese-based oxide or sodium periodate ($NaIO_4$) as oxidants, which are hazardous to the environment and require special disposal procedures.[6,7] In this aspect, the Oppenauer-type oxidation of alcohols (alcohol transfer oxidation) is a desirable method, in which acetone is used not only as a hydrogen acceptor but also as the solvent.[8,9] In the past two decades, transition metal complexes such as Ir,[10]

Ru,[11] Fe[12]-catalyzed Oppenauer-type reactions have gained great attention. Among these transition metal complexes, Ru-based catalysts were widely investigated and were found to be highly efficient. For example, Nishibayashi et al have documented the use of chiral ferrocenyloxazolinylphosphine-ruthenium complex (**a** in Chart 1) as the catalyst for oxidative kinetic resolution of racemic secondary alcohols.[13] In 2014, Wang et al reported an NNC-pincer Ru (II) complex (**b** in Chart 1), which was proven to be an efficient catalyst for the Oppenauer-type oxidation of secondary alcohols.[11b] Recently, Kühn and Baratta used a N-heterocyclic carbene (NHC) ruthenium catalyst (**c** in Chart 1) for the Oppenauer-type oxidation of alcohols and transfer hydrogenation of ketones.[14] However, most of the Ru complexes applied contain phosphine ligands, which require multistep synthesis and may be sensitive to air. Thus, the development of highly active phosphine-free ligand-based Ru complexes for such reaction is still urgent.

Transition-metal carbonyl complexes as a potent catalyst have attracted much attention in organic chemistry due to their high catalytic activity and good stability.[15,16] Moore et al reported the pyridyl-based Ru_3 clusters as an efficient catalyst for the acylation of pyridine.[17] Singh et al introduced the synthesis of secondary amines catalyzed by $Ru_3(hep)_2(CO)_8$ (hep-H = 2-(2-hydroxyethyl) pyridine) clusters.[18] We recently reported a series of pyridine-alcohol and salicylaldiminato-supported trinuclear ruthenium carbonyl complexes as catalysts for the oxidation of alcohols and synthesis of amides and nitriles.[19] Herein, we report the synthesis of trinuclear ruthenium clusters bearing indolyl-pyridinyl-alcohol ligands for Oppenauer-type oxidation of secondary alcohols.

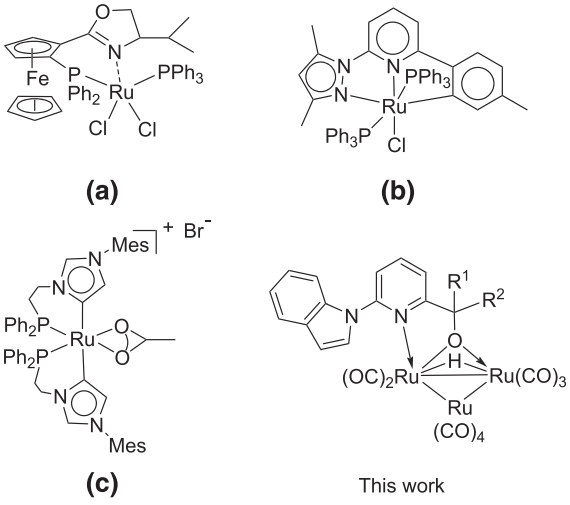


CHART 1 Selected ruthenium complexes for Oppenauer-type oxidation reactions

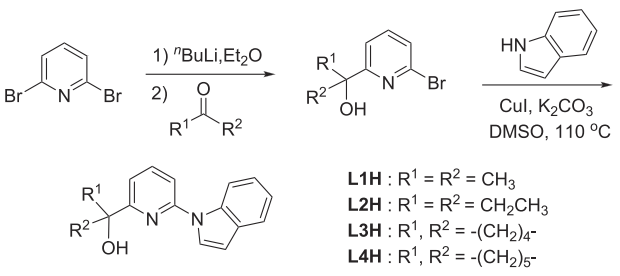
2 | RESULTS AND DISCUSSION

2.1 | Synthesis and characterization of 2-indolyl-6-pyridinyl-alcohol ligands

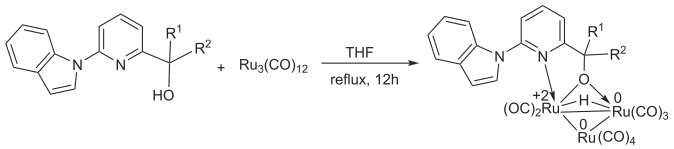
Monolithiation reaction of 2,6-dibromopyridine at −78°C in diethyl ether gave the corresponding 2-lithiopyridine salts, which further reacted with diversely substituted ketones to yield a series of 2-bromopyridine-alcohols compounds. Next, the Ullmann condensation reaction of these compounds with benzopyrrole catalyzed by CuI/K_2CO_3 system at 110°C in DMSO for 12 h generated the 2-indolyl-6-pyridinyl-alcohol ligands **L1H–L4H** in 64%–86% yields (Scheme 1). The ^1H NMR spectra of **L1H-L4H** show a singlet at 4.43, 4.71, 4.25, and 4.26 ppm, respectively, which is assigned to the characteristic hydroxyl proton. The IR spectra of **L1H–L4H** all have a strong broad absorption band at ca. 3300 cm^{-1} owing to the stretching vibration of the O—H bond. The electrospray ionization mass spectrometry (ESI-MS) analyses revealed signals at $m/z = 253.3$ (**L1H**), 281.1 (**L2H**) 279.0 (**L3H**), and 293.1 (**L4H**) corresponding to the cation mass fragments $[M + H]^+$.

2.2 | Synthesis and characterization of ruthenium clusters 1a–1d

Thermal treatment of 2-indolyl-6-pyridinyl-alcohol ligands **L1H–L4H** with $Ru_3(CO)_{12}$ in refluxing THF gave the ruthenium carbonyl complexes $[2\text{-}(C_8H_6N)\text{-}6\text{-}(CR^1R^2O)C_5H_3N](\mu_2\text{-}H)Ru_3(CO)_9$ ($R^1 = R^2 =$ Me (**1a**); $R^1 = R^2 = C_2H_5$ (**1b**); R^1, $R^2 = -(CH_2)_4$- (**1c**); R^1, $R^2 = -(CH_2)_5$- (**1d**)), respectively in 70%–85% yields (Scheme 2). All of these Ru complexes were isolated as air-stable solids and well characterized by NMR spectroscopy, IR, and elemental analysis. The absence of hydroxyl proton in the ^1H NMR spectra of **1a–1d** indicated the successful generation of the Ru—O bond via deprotonation. The characteristic singlet around −12 ppm could be ascribed to Ru—H resonance, which confirmed the presence of



SCHEME 1 Synthesis of indolyl-pyridinyl-alcohol ligands **L1H–L4H**



SCHEME 2 Synthesis of trinuclear ruthenium clusters

TABLE 1 Summary of the crystal data for compound **1a**, **1c**, and **1d**

Complex	1a	1c	1d
Formula	$C_{25}H_{16}N_2O_{10}Ru_3$	$C_{27}H_{18}N_2O_{10}Ru_3$	$C_{28}H_{20}N_2O_{10}Ru_3$
Formula weight	807.61	833.64	847.67
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	9.8933 (8)	9.6057 (5)	9.297 (2)
b (Å)	15.1293 (13)	15.3825 (8)	9.8564 (18)
c (Å)	18.9675 (15)	19.0049 (9)	31.950 (7)
α (°)	90	90	90
β (°)	92.828 (3)	92.724 (5)	90.02 (2)
γ (°)	90	90	90
V (Å^3)	2835.6 (4)	2805.0 (2)	2927.8 (11)
Z	4	4	4
D_{calc} (mg/m^3)	1.892	1.974	1.923
μ (mm^{-1})	1.634	1.655	1.587
F (000)	1568	1624	1656
θ_{max} (°)	25.02	24.998	24.999
Collected reflns	13,846	12,021	12,883
Uniq reflns	4999	4942	5136
R_{int}	0.0291	0.0346	0.1022
GOF	1.083	1.057	1.051
R_1	0.0523	0.0422	0.1282
wR_2	0.0657	0.0700	0.2672
Largest diff peak, hole (e Å^{-3})	0.96 and −0.436	0.68 and −0.800	2.512 and −1.453

hydride in the structure and explained their diamagnetic nature in the ^{1}H NMR spectra. The ^{13}C chemical shifts located in the range of 186–204 ppm confirmed the existence of several carbonyl groups. Every IR spectrum of **1a–1d** displays five strong absorption bands corresponding to the terminal carbonyls. The disappearance of the broad peaks around 3300 cm^{-1} of the free ligands **L1H–L4H** also indicated the binding of the hydroxyl oxygen atom to the ruthenium center.

2.3 | Crystal structures of 1a, 1c, and 1d

The solid-state structures of **1a**, **1c**, and **1d** were further determined by single-crystal crystallography. The crystallographic data, collection parameters, and refinement parameters are listed in Table 1. Their molecular structures are depicted in Figures 1–3 together with selected bond distances and angles, respectively. The ^{1}H NMR spectra clearly indicated the presence of Ru—H bond in the complexes. Thus, the hydride was added during the crystal refinement as a μ_2-H atom, which is similar to the compound $\{\mu^3$-η^2:η^4:η^5-$(C_5H_4N)(C_9H_5)(C{=}CPhCH{=}CPh)\}(\mu_2$-H)$Ru_3(CO)_6$ reported in the literature.[20] As shown, all the three complexes consist of a trinuclear cluster coordinated by an indolyl-pyridinyl-alcohol ligand, and the three Ru atoms form an isosceles triangle. The Ru-Ru distances of **1a**, **1c**, and **1d** are in the range of 2.74–2.81 Å, which are similar to those in our previously reported Ru complexes[21] (2.74–2.82 Å)

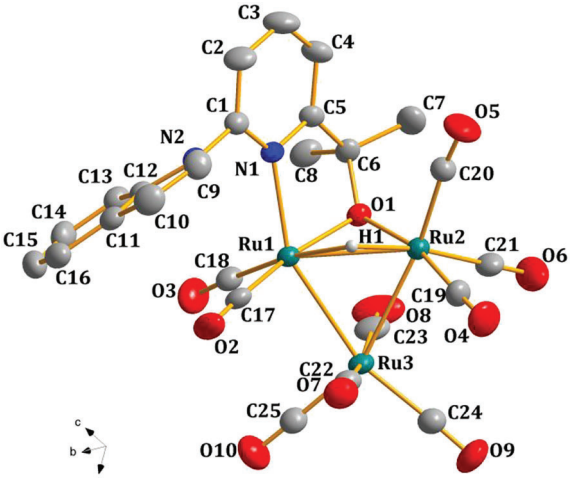


FIGURE 1 Perspective view of **1a** (CCDC: 1939064) with thermal ellipsoids drawn at 50% probability level. Hydrogens are omitted for clarity. The selected bond lengths (Å) and angles (°): Ru(1)-N(1) 2.235(3), Ru(1)-O(1) 2.085(3), Ru(2)-O(1) 2.120(3), Ru(1)-Ru(2) 2.7620(5), Ru(2)-Ru(3) 2.8127(5), Ru(1)-Ru(3) 2.7538(5). Ru(1)-Ru(3)-Ru(2) 59.485(13), Ru(1)-O(1)-Ru(2) 82.12(10), O(1)-Ru(1)-Ru(2) 49.49(7), O(1)-Ru(2)-Ru(1) 48.40(8)

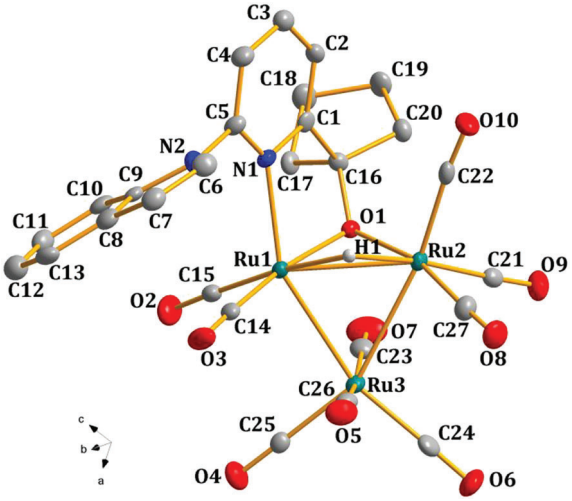


FIGURE 2 Perspective view of **1c** (CCDC: 2040935) with thermal ellipsoids drawn at 30% probability level. Hydrogens are omitted for clarity. The selected bond lengths (Å) and angles (°): Ru(1)-N(1) 2.222(3), Ru(1)-O(1) 2.071(3), Ru(2)-O(1) 2.112(2), Ru(1)-Ru(2) 2.7621(5), Ru(2)-Ru(3) 2.8128(5), Ru(1)-Ru(3) 2.7491(5). Ru(1)-Ru(3)-Ru(2) 59.539(12), Ru(1)-O(1)-Ru(2) 82.65(10), O(1)-Ru(1)-Ru(2) 49.31(7), O(1)-Ru(2)-Ru(1) 48.04(8)

and slightly longer than that of ~2.73 Å in the $Ru_3(CO)_8(\mu\text{-}OC_6H_4OMe\text{-}2)_2$ complex.[22] The Ru—O bond lengths in **1a**, **1c**, and **1d** (2.085(3) Å, 2.071(3) Å, and 2.090(9) Å, respectively) are consistent with that of 2.076(3) Å in $(PyCMe_2O)Ru_3(CO)_8$ complex.[19a] The Ru—N bond distances (2.235(3) Å for **1a**, 2.222(3) Å for

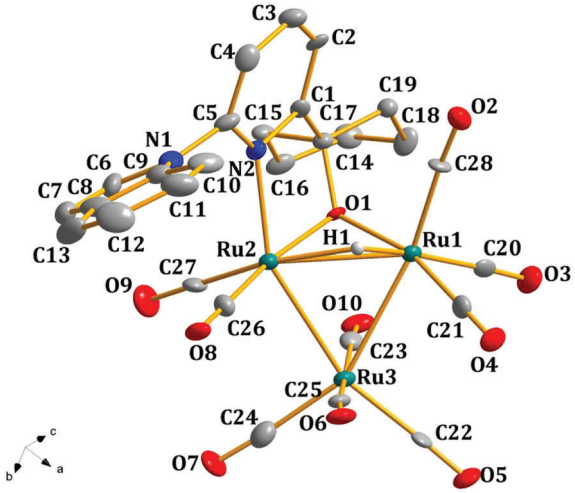


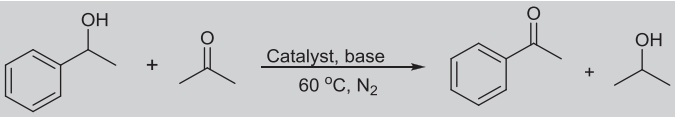
FIGURE 3 Perspective view of **1d** (CCDC: 2040871) with thermal ellipsoids drawn at 50% probability level. Hydrogens are omitted for clarity. The selected bond lengths (Å) and angles (°): Ru(2)-N(2) 2.200(13), Ru(2)-O(1) 2.090(9), Ru(1)-O(1) 2.147(9), Ru(2)-Ru(1) 2.7454(16), Ru(1)-Ru(3) 2.8012(17), Ru(2)-Ru(3) 2.7459(17). Ru(2)-Ru(3)-Ru(1) 59.32(4), Ru(2)-O(1)-Ru(1) 80.8(3), O(1)-Ru(2)-Ru(1) 50.5(2), O(1)-Ru(1)-Ru(2) 48.7(2)

1c, and 2.200(13) Å for **1d**, respectively) are in the normal range and are also close to the pyridine-based Ru clusters.[18,23]

2.4 | Catalytic activities of new trinuclear ruthenium complexes

We chose 1-phenylethanol as the model substrate and ruthenium complex **1a** as the catalyst in Oppenauer-type oxidation to screen the reaction conditions. The results are summarized in Table 2. Initially, various bases were screened and employment of different bases indicated Na_2CO_3 was the best one to give the acetophenone in maximum yield of 91% (Table 2, entries 1–8). Next, the catalyst loading effect on the reaction was examined. Reducing the loading of **1a** from 1.0 to 0.5 mol% resulted in the decrease of the yield of acetophenone from 91% to 72% (entry 9). A substantial drop in yield was also observed when the amount of Na_2CO_3 was reduced from 1.0 to 0.5 mmol (entry 10). Extension of reaction duration from 8 to 10 h did not improve the yield efficiently, whereas shortening the time to 6 h lowered the yield to 82% (entries 11–12). Subsequently, the control experiments showed that without catalyst or base, the oxidation reaction either did not occur or gave very low yield (entries 13–14). Furthermore, lowering the reaction temperature to 50°C led to 73% yield of acetophenone (entry 15). Finally, the other three Ru complexes **1b–1d** were also examined under the optimized conditions mentioned above. As shown, **1b–1d** displayed

TABLE 2 Screening of condition for the Oppenauer-type oxidation of 1-phenylethanol



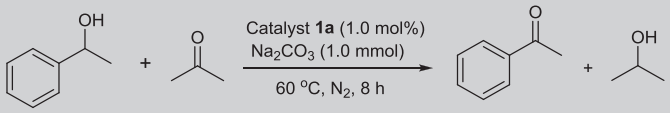
Entry	Cat. (mol%)	Base	Time (h)	Yield (%)[a]
1	**1a** (1.0)	Et_3N	8	47
2	**1a** (1.0)	*t*-BuONa	8	53
3	**1a** (1.0)	*t*-BuOK	8	60
4	**1a** (1.0)	DABCO	8	43
5	**1a** (1.0)	Cs_2CO_3	8	65
6	**1a** (1.0)	K_2CO_3	8	83
7	**1a** (1.0)	$NaHCO_3$	8	80
8	**1a** (1.0)	Na_2CO_3	8	91
9	**1a** (0.5)	Na_2CO_3	8	72
10[b]	**1a** (1.0)	Na_2CO_3	8	78
11	**1a** (1.0)	Na_2CO_3	10	92
12	**1a** (1.0)	Na_2CO_3	6	82
13	—	Na_2CO_3	8	—
14	**1a** (1.0)	—	8	12
15[c]	**1a** (1.0)	Na_2CO_3	8	73
16	**1b** (1.0)	Na_2CO_3	8	87
17	**1c** (1.0)	Na_2CO_3	8	80
18	**1d** (1.0)	Na_2CO_3	8	75
19	**$Ru_3(CO)_{12}$** (1.0)	Na_2CO_3	8	41

Note: Reaction conditions: 1-phenylethanol (1.0 mmol), acetone (5.0 ml), and base (1.0 mmol).
[a]Determined by GC analysis (average of two trials).
[b]Na_2CO_3 (0.5 mmol).
[c]Temperature = 50°C.

good catalytic activities achieving decent yields of 75%–87% (entries 16–18). But the complex **1a** with methyl substituents showed the best catalytic activity. This may be due to the small steric hindrance of the methyl groups, which is beneficial to the coordination of the substrate to the metal ruthenium atom. For comparison, $Ru_3(CO)_{12}$ was also tested as a catalyst under the same conditions, but only gave 41% yield (entry 19), indicating the ligands play an important role in the homogeneous catalytic system. Thus, the optimized conditions for the Oppenauer-type oxidation of 1-phenylethanol are as follows: **1a** (1.0 mol%) as the catalyst, acetone as the oxidant and solvent, and Na_2CO_3 (1 equivalent) as the base, at a temperature of 60°C and reaction for 8 h.

With the optimized reaction conditions in hand, we sought to explore the generality and limitation of the present catalytic system. The results for the oxidation of secondary alcohols are summarized in Table 3. As shown, acetophenones bearing electron-donating methyl and methoxy substituents gave rise to the desired products in yields between 88% and 92% (Table 3, entries 1–4) regardless of whether the group was at an ortho, meta, or para position, showing no obvious steric effect. The electron-withdrawing groups such as chloro and bromo on the acetophenone formed the corresponding ketones in relatively low yields of 70%–80% (entries 5–8), indicating that the electronic nature of substituents had some effects on product yields. We were pleased to observe that the catalytic system worked well for sterically hindered alcohols (e.g., 1-(2-naphthyl)ethanol, diphenylmethanol, 9H-fluoren-9-ol, and benzoin) (entries 9–12). Fused benzyl alcohols such as 1-tetralol and 1-indanol, under these conditions, also afforded the corresponding ketones in high yield (94% and 92%, respectively, entries 13 and 14). Furthermore, Ru cluster **1a** could chemoselectively oxidized the secondary alcohol moiety in 1-phenyl-1,2-ethanediol to produce the hydroxyacetophenone in 80% yield (entry 15), displaying good chemoselectivity of the present catalytic system. Non-benzyl alcohols including cyclic alcohols and linear aliphatic alcohols were also efficiently

TABLE 3 Oppenauer-type oxidations of alcohols catalyzed by complex **1a**



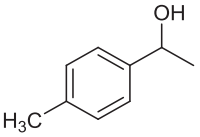
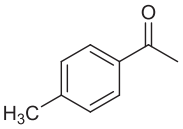
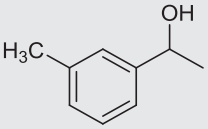
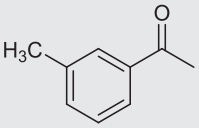
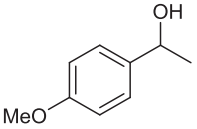
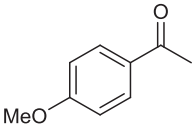
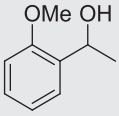
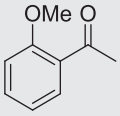
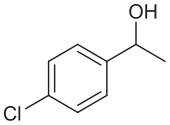
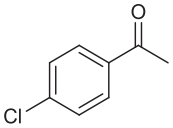
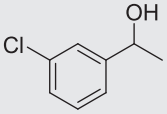
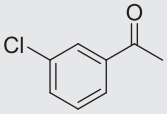
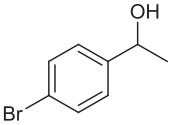
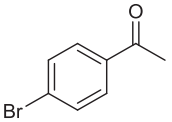
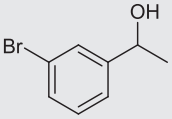
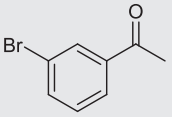
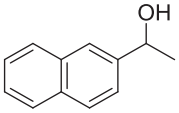
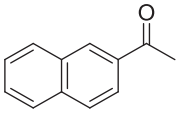
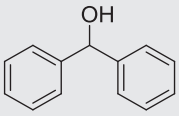
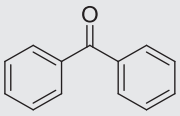
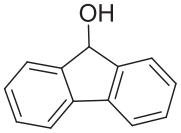
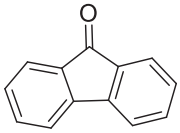
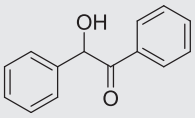
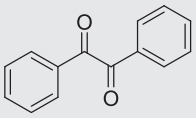
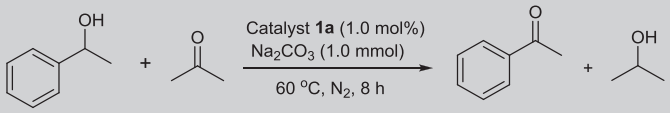
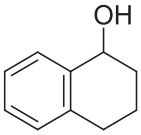
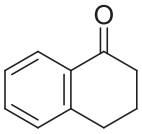
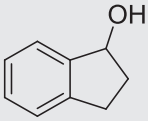
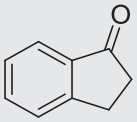
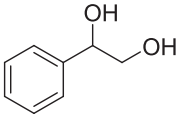
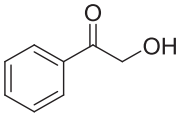
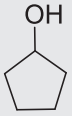
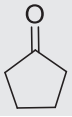
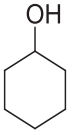
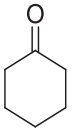
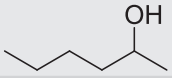
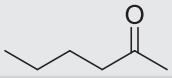
Entry	Substrate	Time (h)	Yield (%)[a]
1			92
2			90
3			91
4			88
5			80
6			77
7			75
8			70
9			90
10			92
11			88
12			83

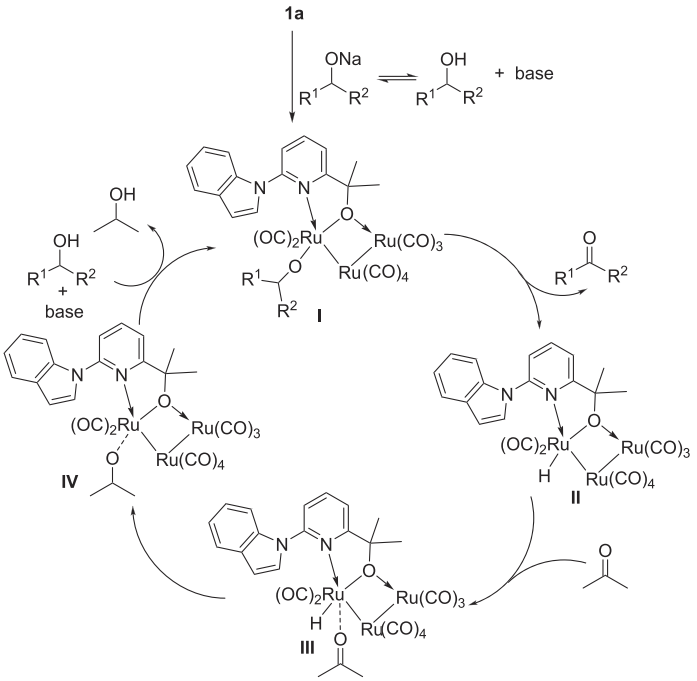
TABLE 3 (Continued)



Entry	Substrate	Time (h)	Yield (%)[a]
13			94
14			92
15			80
16			83
17			85
18			81

Note: Reaction conditions: secondary alcohol (1.0 mmol) and acetone (5.0 ml).
[a]Determined by GC analysis (average of two trials).

SCHEME 3 Proposed mechanism for Ru-catalyzed Oppenauer-type oxidation of secondary alcohols



oxidized to the corresponding ketones in >80% yields under the same conditions without using a higher loading of catalyst or extending the reaction time (entries 16–18).

Taken previous reports into account,[11,17] a plausible mechanism was proposed in Scheme 3 based on trinuclear pathway. Initially, **1a** reacted with sodium alkoxide (from substrate alcohol and NaOH) to give the Ru-alkoxide species **I**, which underwent β-elimination to form Ru—H intermediate **II** and ketone product. Then, coordination of acetone to the in-situ generated Ru—H species gave species **III**, which upon insertion of the ketone into the Ru—H bond, gave the Ru-alkoxide species **IV**. Finally, base-promoted alcohol metathesis with **IV** regenerated species **I** and finished the catalytic cycle. It should be pointed out that the possibility of non-trinuclear Ru carbonyl species being involved in the catalytic reaction cannot be ruled out.

3 | CONCLUSION

In conclusion, we have synthesized a series of indolyl-pyridinyl-alcohol ligand-coordinated trinuclear ruthenium clusters by reactions of $Ru_3(CO)_{12}$ with 2-indolyl-6-pyridinyl-alcohol compounds, which were well characterized by NMR, IR, and so on. These Ru complexes exhibit excellent catalytic activity in the Oppenauer-type oxidation of secondary alcohols in the presence of Na_2CO_3, of which complex **1a** is the most active. These catalysts are easy to synthesize and stable to air and moisture. The present catalytic system features broad substrate scope, high catalytic activity, low catalyst loading and good chemoselectivity.

4 | EXPERIMENTAL

4.1 | General considerations

All manipulations were carried out under an argon atmosphere using a Schlenk line. The solvents were dried and distilled prior to use by the literature methods. All reagents purchased commercially were used directly without further purification. ^{1}H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded on a Zhongke-Niujin Quantum-I 400 spectrometer. Elemental analyses were performed using a Vario EL III analyzer. IR spectra were recorded as KBr disks on a Thermo Fisher iS50 spectrometer. Mass spectroscopy was performed with an AB SCIEX 3200 Q-TRAP mass spectrometer. GC measurements were performed on Agilent GC7890B equipment using an Agilent DB-FFAP (30 m × 320 μm) column. $Ru_3(CO)_{12}$ was synthesized according to the literature.[24] 2-Bromopyridyl alcohol compounds were synthesized according to the literature.[25]

4.2 | Synthesis of 2-(C_8H_6N)-6-(CMe_2OH) C_5H_3N (L1H)

Under a N_2 atmosphere, a mixture of 2-(6-bromopyridin-2-yl)propan-2-ol (1.21 g, 5.5 mmol), indole (0.43 g, 3.7 mmol), CuI (0.07 g, 0.36 mmol), and K_2CO_3 (1.01 g, 7.3 mmol) in 30 ml of DMSO was stirred at 110°C for 12 h. After cooled to room temperature, 10 ml of brine was added to the mixture, and the solution was extracted with dichloromethane (3 × 15 ml). The combined organic phase was dried with Na_2SO_4, and then, the solvent was removed under reduced pressure. The obtained product was purified by column chromatography (Al_2O_3, ethyl acetate: petroleum ether = 1:10) to give **L1H** as a red oil (0.80 g, 86% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.11 (d, J = 8.3 Hz, 1H, Py-*H*), 7.81 (t, J = 7.9 Hz, 1H, Py-*H*), 7.67 (d, J = 7.8 Hz, 2H, Ar-*H*, Py-*H*), 7.35 (d, J = 8.0 Hz, 1H, Ar-*H*), 7.29 (d, J = 8.0 Hz, 1H, Ar-*H*), 7.23 (d, J = 5.6 Hz, 1H, Ar-*H*), 7.21 (s, 1H, Ar-*H*), 6.72 (s, 1H, Ar-*H*), 4.43 (s, 1H, O*H*), 1.62 (s, 6H, C*H*$_3$) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 166.2, 150.8, 139.6, 134.9, 130.4, 126.1, 121.2, 112.8, 105.5, 72.4, 40.8, 30.6 ppm. MS (ESI, *m/z*): 253.3 $[M + H]^+$.

4.3 | Synthesis of 2-(C_8H_6N)-6-[C (C_2H_5)$_2$OH]C_5H_3N (L2H)

Following the procedure for **L1H**, from 3-(6-bromopyridin-2-yl)pentan-3-ol, **L2H** was obtained as a red oil (0.66 g, 64% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.10 (d, J = 8.3 Hz, 1H, Py-*H*), 7.81 (d, J = 10.4 Hz, 1H, Py-*H*), 7.72–7.62 (m, 2H, Ar-*H*, Py-*H*), 7.35–7.28 (m, 2H, Ar-*H*), 7.22 (d, J = 9.3, 1H, Ar-*H*), 7.18–7.10 (m, 2H, Ar-*H*), 6.72 (d, J = 3.4 Hz, 1H, Ar-*H*), 4.71 (s, 1H, O*H*), 2.03–1.79 (m, 4H, CH_2), 0.94–0.62 (m, 6H, CH_3). ppm.^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 163.7, 150.6, 139.4, 135.0, 130.5, 126.2, 121.4, 112.5, 105.7, 34.7, 7.9 ppm. MS (ESI, *m/z*): 281.1 $[M + H]^+$.

4.4 | Synthesis of 2-(C_8H_6N)-6-[C (CH_2)$_4$OH]C_5H_3N (L3H)

Following the procedure for **L1H**, from 1-(6-bromopyridin-2-yl)cyclopentan-1-ol, **L3H** was obtained as a red oil (0.73 g, 71% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.11 (d, J = 8.3 Hz, 1H, Py-*H*), 7.80 (t, J = 7.9 Hz, 1H,

Py-*H*), 7.72–7.61 (m, 2H, Ar-*H*, Py-*H*), 7.36–7.28 (m, 2H, Ar-*H*), 7.22 (d, $J = 9.9$ Hz, 2H, Ar-*H*), 6.70 (s, 1H, Ar-*H*), 4.25 (s, 1H, O*H*), 1.83 (d, $J = 25.1$, 8H, cyclopentyl-*H*) ppm.^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 166.3, 150.7, 139.5, 134.9, 130.4, 126.1, 121.2, 114.1, 110.7, 105.6, 73.4, 38.4, 22.1 ppm. MS (ESI, *m/z*): 279.0 $[M + H]^+$.

4.5 | Synthesis of 2-(C_8H_6N)-6-[C (CH_2)$_5$OH]C_5H_3N (L4H)

Following the procedure for **L1H**, from 1-(6-bromopyridin-2-yl)cyclohexan-1-ol, **L4H** was obtained as a red oil (0.79 g, 73% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.12 (d, $J = 8.1$ Hz, 1H, Py-*H*), 7.84 (t, $J = 7.9$ Hz, 1H, Py-*H*), 7.69 (d, $J = 5.6$ Hz, 2H, Ar-*H*, Py-*H*), 7.37 (d, $J = 8.0$ Hz, 1H, Ar-*H*), 7.33–7.27 (m, 2H, Ar-*H*), 7.21 (t, $J = 7.2$ Hz, 1H, Ar-*H*), 6.72 (d, $J = 3.3$ Hz, 1H, Ar-*H*), 4.26 (s, 1H, O*H*), 2.00–1.63 (m, 10H, cyclohexyl-*H*) ppm.^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 166.3, 150.8, 139.5, 134.9, 130.4, 123.2, 121.2, 115.2, 112.7, 105.5, 73.3, 38.4, 25.6, 22.1 ppm. MS (ESI, *m/z*): 293.1 $[M + H]^+$.

4.6 | Synthesis of 1a

Under a N_2 atmosphere, a mixture of **L1H** (0.08 g, 0.32 mmol), $Ru_3(CO)_{12}$ (0.21 g, 0.32 mmol), in 20 ml of THF was refluxed for 12 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was purified by column chromatography on Al_2O_3 (ethyl acetate: petroleum ether = 1: 20) to give **1a** as a yellow solid (0.11 g, 43% yield). Anal. Calc. for $C_{25}H_{16}N_2O_{10}Ru_3$: C, 37.18; H, 2.00; N, 3.47. Found (%): C, 37.43; H, 1.77; N, 3.65. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.11 (d, $J = 8.3$ Hz, 1H, Py-*H*), 7.81 (t, $J = 7.9$ Hz, 1H, Py-*H*), 7.68 (d, $J = 5.6$ Hz, 2H, Ar-*H*, Py-*H*), 7.37–7.20 (m, 4H, Ar-*H*), 6.71 (d, $J = 3.4$ Hz, 1H, Ar-*H*), 1.62 (s, 6H, C*H*$_3$), −11.98 (s, 1H, Ru-*H*) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 203.8, 199.4, 199.0, 197.3, 197.2, 193.3, 190.3, 185.9, 168.2, 139.7, 136.0, 129.8, 127.4, 123.3, 121.7, 119.2, 111.0, 106.7, 102.7, 89.1, 34.1, 31.3 ppm. IR (υ_{CO}, KBr, cm^{-1}): 2095(s), 2051(s), 2001(s), 1970(s), 1931(s).

4.7 | Synthesis of 1b

The preparation of **1b** was carried out using a procedure and molar ratios similar to those described for the synthesis of **1a** but with **L2H** as the ligand. Complex **1b** was obtained as a yellow solid (0.09 g, 34% yield). Anal. Calc. for $C_{27}H_{20}N_2O_{10}Ru_3$: C, 38.81; H, 2.41; N, 3.35. Found (%): C, 38.67; H, 2.17; N, 3.11. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.74 (t, $J = 7.8$ Hz, 1H, Py-*H*), 7.67 (d, $J = 7.8$ Hz, 1H, Py-*H*), 7.58 (d, $J = 7.9$ Hz, 1H, Py-*H*), 7.32 (d, $J = 8.1$ Hz, 1H, Ar-*H*), 7.24–7.17 (m, 2H, Ar-*H*), 7.15–7.11 (m, 2H, Ar-*H*), 6.82 (d, $J = 3.2$ Hz, 1H, Ar-*H*), 1.13 (d, $J = 13.5$ Hz, 10H, ethyl-*H*), −12.04 (s, 1H, Ru-*H*) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) δ203.5, 197.0, 193.6, 186.1, 139.0, 135.8, 129.9, 127.8, 124.1, 122.0, 121.8, 121.6, 120.7, 119.8, 111.0, 102.7, 93.7, 29.7, 6.7 ppm. IR (υ_{CO}, KBr, cm^{-1}): 2092(s), 2045(s), 2016(s), 1985(s), 1935(s).

4.8 | Synthesis of 1c

The preparation of **1c** was carried out using a procedure and molar ratios similar to those described for the synthesis of **1a** but with **L3H** as the ligand. Complex **1c** was obtained as a yellow solid (0.09 g, 34% yield). Anal. Calc. for $C_{27}H_{18}N_2O_{10}Ru_3$: C, 38.90; H, 2.18; N, 3.36. Found (%): C, 39.14; H, 1.92; N, 3.15. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.84 (t, $J = 7.8$ Hz, 1H, Py-*H*), 7.75 (d, $J = 7.7$ Hz, 1H, Py-*H*), 7.40–7.22 (m, 6H, Ar-*H*, Py-*H*), 6.90 (d, $J = 3.3$ Hz, 1H, Ar-*H*), 2.50–2.33 (m, 2H cyclopentyl-*H*), 2.21–2.09 (m, 2H, cyclopentyl-*H*), 1.96 (d, $J = 14.9$ Hz, 2H, cyclopentyl-*H*), 1.75 (s, 2H, cyclopentyl-*H*), −11.84 (s, 1H, Ru-*H*) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 203.8, 199.5, 197.5, 193.4, 190.3, 185.7, 167.9, 139.7, 136.1, 132.4, 130.9, 128.9, 127.5, 123.3, 121.6, 118.8, 101.3, 65.6, 45.7, 42.8, 30.6, 29.7, 24.5, 24.0, 19.2, 13.7 ppm. IR (υ_{CO}, KBr, cm^{-1}): 2094(s), 2052(s), 2017(s), 1969(s), 1932(s).

4.9 | Synthesis of 1d

The preparation of **1d** was carried out using a procedure and molar ratios similar to those described for the synthesis of **1a** but with **L4H** as the ligand. Complex **1d** was obtained as a yellow solid (0.10 g, 37% yield). Anal. Calc. for $C_{28}H_{20}N_2O_{10}Ru_3$: C, 39.67; H, 2.38; N, 3.31. Found (%): C, 39.87; H, 2.27; N, 3.05. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ 7.85–7.77 (m, 1H, Py-*H*), 7.72 (t, $J = 8.2$ Hz, 1H, Py-*H*), 7.55–7.27 (m, 6H, Ar-*H*), 6.89 (d, $J = 3.1$ Hz, 1H, Ar-*H*), 2.32–2.10 (m, 2H, cyclohexyl-*H*), 2.09–1.91 (m, 4H, cyclohexyl-*H*), 1.86–1.76 (m, 2H, cyclohexyl-*H*), 1.56 (s, 2H cyclohexyl-*H*), −12.20 (s, 1H, Ru-*H*) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 204.3, 199.4, 197.7193.4, 189.9, 186.3, 169.2, 139.6, 135.6, 130.9, 130.1, 127.2, 126.9, 123.3, 121.7, 118.9, 107.0, 43.7, 38.1, 25.6,

21.7 ppm. IR (υ_{CO}, KBr, cm^{-1}): 2091(s), 2046(s), 2027 (s), 1982(s), 1931(s).

4.10 | General procedure for the Oppenauer-type oxidation of secondary alcohols

Under a N_2 atmosphere, a mixture of 1-phenylethanol (0.122 g, 1.0 mmol), complex **1a** (0.008 g, 0.01 mmol) and Na_2CO_3 (0.10 g, 1.0 mmol) in 5 ml of acetone was stirred at 60°C for 8 h. After it cooled to ambient temperature, 0.1 ml of the reaction mixture was sampled for GC analysis. The resultant solution was condensed under reduced pressure and subjected to purification by column chromatography on Al_2O_3 (ethyl acetate: petroleum ether = 1: 15) to give the corresponding acetophenone as a yellow oily liquid (0.10 g, 85% yield), which was further identified by comparison with the authentic sample through NMR.

4.11 | X-ray crystal structural determination

Single crystals of **1a**, **1c**, and **1d** suitable for X-ray diffraction analysis were obtained from a CH_2Cl_2/hexane mixed solution at room temperature. Data were collected on a Bruker SMART 1000 CCD diffractometer and Oxford Diffraction SuperNova dual source diffractometers with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using Olex2 software[26] and SHELXTL program package.[27] All nonhydrogen atoms were refined anisotropically, and all hydrogen atoms were placed in calculated positions. The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers CCDC 1939064 for **1a**, CCDC 2040935 for **1c**, and CCDC 2040871 for **1d**.

ACKNOWLEDGMENTS

This work was supported by the Hebei Natural Science Foundation of China (B2017205006 and B2019205087), the Education Department Foundation of Hebei Province (ZD2018005 and QN2019036), and the Science Foundation of Hebei Normal University (L2017Z02 and L2018B08).

AUTHOR CONTRIBUTIONS

Qing Dong: Data curation; investigation; methodology. **Zongwen Ma:** Investigation; methodology. **Zhiqiang Hao:** Funding acquisition; supervision. **Zhangang Han:** Formal analysis; methodology. **jin lin:** Project administration; supervision; validation. **Guo-Liang Lu:** Formal analysis; methodology.

CONFLICT OF INTEREST

There are no conflicts to declare.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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How to cite this article: Q. Dong, Z. Ma, Z. Hao, Z. Han, J. Lin, G.-L. Lu, *Appl Organomet Chem* **2021**, e6336. https://doi.org/10.1002/aoc.6336