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Authors: Zhiqiang Hao, Kang Liu, Qi Feng, Qing Dong, Dongzhu Ma,* Zhangang Han, Guo-Liang Lu, and Jin Lin*

Ruthenium(II) complexes bearing Schiff base ligands for the efficient acceptorless dehydrogenation of secondary alcohols[†]

Zhiqiang Hao,[a] Kang Liu,[a] Qi Feng,[a] Qing Dong,[a] Dongzhu Ma,*,[b] Zhangang Han,[a] Guo-Liang Lu,[c] and Jin Lin*,[a]

[a] Hebei Key Laboratory of Organic Functional Molecules, The College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang 050024, China
[b] Department of environment and chemical engineering, Hebei College of Industry and Technology, Shijiazhuang 050091, China
[c] Auckland Cancer Society Research Centre, Faculty of Medical and Health Sciences, The University of Auckland, Private Bag 92019, Auckland 1142, New Zealand

Summary of main observation and conclusion   Four ruthenium(II) complexes **1—4** [RN=CH-(2,4-(^{t}Bu)$_2$C$_6$H$_2$O)]RuH(PPh$_3$)$_2$(CO) (R = C$_6$H$_5$, **1**; R = 4-MeC$_6$H$_4$, **2**; R = 4-ClC$_6$H$_4$, **3**; R = 4-BrC$_6$H$_4$, **4**) bearing Schiff base ligand were prepared by treating RuHClCO(PPh$_3$)$_3$ with RN=CH-(2,4-(^{t}Bu)$_2$C$_6$H$_2$OH (**L1—L4**) in the presence of triethylamine. Their structures were fully characterized by elemental analysis, IR, NMR spectroscopy and X-ray crystallography. These Ru(II) complexes exhibit high catalytic performance and good functional-group compatibility in the acceptorless dehydrogenation of secondary alcohols, affording the corresponding ketones in 82—94% yields.

Background and Originality Content

Efficient oxidation of alcohols to aldehydes or ketones is a pivotal reaction in organic synthesis.[1-3] The corresponding carbonyl compounds are the key and versatile intermediates for the synthesis of a wide range of fine and pharmaceutical chemicals.[4-5] Classical methods for this transformation use stoichiometric oxidants such as hypochlorite,[6] manganese salts,[7] and hypervalent iodines,[8] etc., and produce large amounts of toxic wastes or undesirable by-products. Catalytic systems for this transformation operate with molecular oxygen[9,10] or H$_2$O$_2$[11] as environmentally friendly oxidants have also been reported. However, additives like TEMPO (2,2,6,6-tetramethylpiperidyl-l-oxy) or carboxylic acids are required to accelerate the reactions. Besides, ketones and aldehydes can also be synthesized via the oxidation of the C–H or C–X (Cl, Br) bond of alkyl arenes[12] or the oxidation of alkenes.[13] For most of the synthetic approaches described above, oxidizing agents or additives are necessary in order to achieve short reaction time and a high yield, which cause environmental problems. With the increasing focus on environmental problems, the quest for oxidant-free, cost-effective and more green strategies is pressing and highly desirable.
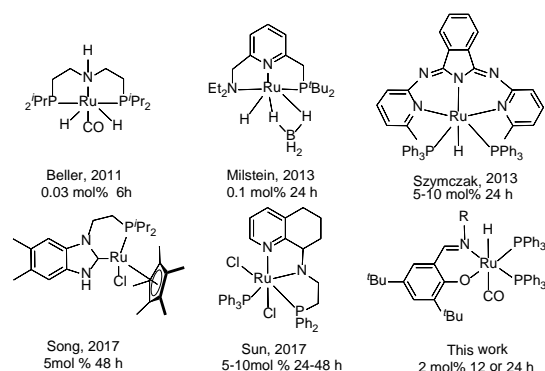

Figure 1 Selected Ru complexes for acceptorless dehydrogenation of secondary alcohols.

Indeed, significant efforts have been made to develop new catalytic protocols in an environmentally friendly manner. In the past decade, acceptorless alcohol dehydrogenation (AAD) reactions have gained major interest and have emerged as an important transformation in synthesising carbonyl compounds without using any oxidants.[14] The advantage of the ADD reactions is that H$_2$ gas is the only by-product, which can be a clean source of energy.[15] Many catalytic systems for such transformation have been reported based on the complexes of noble metals such as Ir,[16] Ru,[17] and Os[18] or nonprecious metals such as Fe[19] and Co.[20] Among the employed transition metal complexes, ruthenium complexes have been intensively studied due to their excellent catalytic performance. In 2011, Beller *et al*. reported the tridentate PNP Ru complexes generated in suit for the dehydrogenation of isopropyl alcohol, giving acetone with high turnover frequency (Figure 1).[21] Subsequently, Milstein's

group successfully developed a Ru-NNP pincer complex for the dehydrogenation of secondary alcohols under base-free condition.[14c] In the same year, Szymcazk and co-workers reported that an NNN-Ru(II) hydride complex is efficient for oxidation of secondary alcohols in the presence of primary alcohols with good chemoselectivity.[22] In 2017, Song *et al*. described the use of N-heterocyclic carbene (NHC) supported Ru complex for the dehydrogenation of secondary alcohols to give ketones in good yield at high temperature (140 °C).[23] Moreover, Sun and Solan explored the catalytic activity of tridentate PNN-Ru catalyst in such reactions to afford the corresponding aromatic and cycloalkyl-containing ketones in refluxing p-xylene.[24] Although these examples for the acceptorless dehydrogenation of secondary alcohols have been proved to be highly useful, most of the reported ruthenium catalysts were focused on using pincer ligands, especially phosphine ligands that are difficult to prepare (through multi-steps) and inconvenient to handle (air and moisture-sensitive). The development of easily-accessed ligands and their stable metal complexes for such transformation under mild condition is still highly desirable. Recently, our group successfully developed a series of pyridyl-alcohol-based Ru complexes that displayed high efficiency for dehydrogenative oxidation of alcohols, producing ketones in excellent yield.[25]

Schiff base compounds are very useful because of their widespread applications in fluorescence properties,[26] catalytic processes[27] and biological activities.[28] Recently, metal complexes of tetradentate and tridentate Schiff bases were screened for their catalytic activity in the oxidation of alcohols with oxygen or other oxidants.[29] However, the complexes containing Schiff base ligands for ADD are rarely reported. In this paper we describe the syntheses of a series of readily available ruthenium hydride complexes stabilized by N,O-bidentate Schiff base ligands and their catalytic behaviour toward the acceptorless dehydrogenation of secondary alcohols under mild condition.

Results and Discussion

Synthesis and characterization of Schiff base ruthenium complexes

The bidentate Schiff base ligands RN=CH-(2,4-(^{t}Bu)$_2$C$_6$H$_2$OH (R = C$_6$H$_5$, **L1**; R = 4-MeC$_6$H$_4$, **L2**; R = 4-ClC$_6$H$_4$, **L3**; R = 4-BrC$_6$H$_4$, **L4**) were synthesized by the condensation reactions of 3,5-di-tert-butyl-2-hydroxybenzaldehyde with the corresponding primary amines in ethanol. Reactions of RuHClCO(PPh$_3$)$_3$ with the Schiff bases in refluxing THF in the presence of triethylamine, afforded the ruthenium(II) complexes **1—4** in isolated yields of 42 ~ 57% (Scheme 1). In these reactions, one PPh$_3$ and the Cl in the starting ruthenium compound were replaced by one molecule of the bidentate Schiff base ligand. It was found the complexes are stable against air and moisture during work-up by column chromatography using undried commercial solvents as eluent.

L1: R = C$_6$H$_5$ **L2**: R = 4-MeC$_6$H$_4$
L3: R = 4-ClC$_6$H$_4$ **L4**: R = 4-BrC$_6$H$_4$ **1-4**
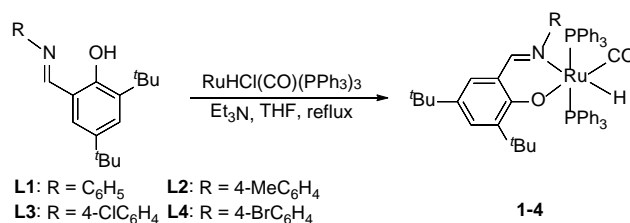
Scheme 1 Synthesis of ruthenium complexes **1—4**.

Complexes **1—4** were fully characterized by routine analyses and single-crystal X-ray diffraction as well. The NMR analyses of the complexes are in agreement with their structure. In the ^{1}H NMR spectra of **1—4**, the OH protons in their free ligand around 8.63 ppm disappeared, suggesting the formation of Ru—O bonds in the finally Ru complexes. The triplet at −10.41 (for **1**), −10.39 (for **2**), and −10.48 ppm (for **3** and **4**) belong to the Ru–H bonds. The ^{31}P{^{1}H} NMR spectra of all the complexes show a singlet at ~41.0 ppm for the two PPh$_3$. The IR spectra of **1—4** display one absorption peak at 1914, 1916, 1919 and 1911 cm^{-1}, respectively, revealing the presence of one terminal CO, which are comparable to those of the similar ruthenium carbonyl complexes reported in the literature.[30] The stretching vibration peaks for Ru—H were found from 2004 to 2053 cm^{-1}.

The molecular structures of **1—4** were further confirmed by X-ray crystallography, as shown in Figures **2—5** with selected bond lengths and angles. The crystallographic data of the four Ru complexes are in Supporting Information (Table S1). In each complex, the Ru ion is coordinated in an octahedral geometry environment surrounded by the bidentate Schiff base ligand, two PPh$_3$, one hydride and one CO. The distance of Ru—H bond in complex **1** (1.55(3) Å) is shorter than that in complex **2** (1.578(19) Å) and longer than those in complexes **3** and **4** (1.463(14) Å and 1.509(19) Å, respectively), which is close to the values in the literature.[31,5a] The N—Ru—H angles of the four Ru complexes are in the range of 159.5(17) ~ 174.6(12)°, indicating the hydride is positioned trans to the imine nitrogen atom. The P—Ru—P axis is approximately linear, as seen in the angles from 166.33(5) to 168.62(4)° in **1—4**. The Ru—O and Ru—N bond lengths in **1—4** are in the average of 2.131(4) and 2.186(4) Å, respectively, which are comparable with those observed in their bis-chelate Ru(II) analogues reported previously.[32]
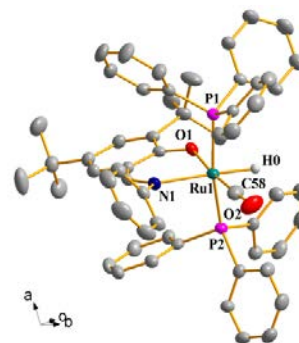
Figure 2 Molecular structure of complex **1** with ellipsoids at 30% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–O(1) 2.140(3), Ru(1)–N(1) 2.192(3), Ru(1)–P(1) 2.3684(12), Ru(1)–P(2) 2.3842(12), Ru(1)–H(0) 1.55(3); O(1)–Ru(1)–N(1) 84.81(12), O(1)–Ru(1)–P(1) 89.14(8), O(1)–Ru(1)–P(2) 85.54(8), P(1)–Ru(1)–P(2) 168.62(4).
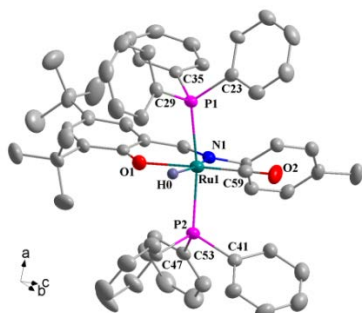

Figure 3 Molecular structure of complex **2** with ellipsoids at 30% probability level. Hydrogen atoms and disordered part were omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–O(1) 2.145(3), Ru(1)–N(1) 2.183(4), Ru(1)–P(1) 2.3893(13), Ru(1)–P(2) 2.3636(13), Ru(1)–H(0) 1.578(19); O(1)–Ru(1)–N(1) 84.66(14), O(1)–Ru(1)–P(1) 84.80(10), O(1)–Ru(1)–P(2) 88.85(10), P(1)–Ru(1)–P(2) 167.39(5).
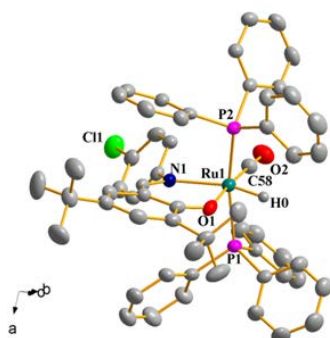

Figure 4 Molecular structure of complex **3** with ellipsoids at 30% probability level. Hydrogen atoms and disordered part were omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–O(1) 2.158(3), Ru(1)–N(1) 2.180(3), Ru(1)–P(1) 2.3617(11), Ru(1)–P(2) 2.3858(11), Ru(1)–H(0) 1.463(14); O(1)–Ru(1)–N(1) 84.33(12), O(1)–Ru(1)–P(1) 88.67(8), O(1)–Ru(1)–P(2) 84.78(8), P(1)–Ru(1)–P(2) 166.36(5).
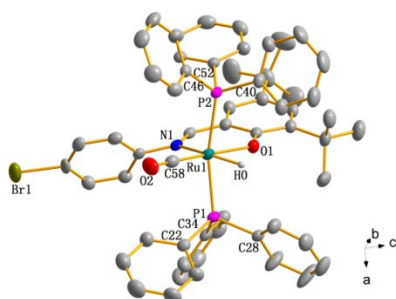

Figure 5 Molecular structure of complex **4** with ellipsoids at 30% probability level. Hydrogen atoms and disordered part were omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–O(1) 2.142(3), Ru(1)–N(1) 2.182(3), Ru(1)–P(1) 2.3593(9), Ru(1)–P(2) 2.3833(10), Ru(1)–H(0) 1.509(19); O(1)–Ru(1)–N(1) 84.66(10), O(1)–Ru(1)–P(1) 88.97(11) 88.73(7), O(1)–Ru(1)–P(2) 84.64(8), P(1)–Ru(1)–P(2) 166.06(4).

Catalytic dehydrogenation of alcohols

We firstly examined the dehydrogenation reaction using 1-phenylethanol (1.0 mmol) as substrate and complex **1** (1.0 mol%) as catalyst in toluene to screen the best base. Employment of inorganic base such as KOH or K_2CO_3 etc. gave the desired product acetophenone in low yield (21~48%, Table S2, entries 1–4). When organic base (e.g. DBU, DABCO or *t*-BuOK) was used, the yield increased remarkably (Table S2, entry 5-7) and *t*-BuOK was found to be much more active than the other bases to give acetophenone in 84% yield. The performance of inorganic bases showed less efficient probably because of the poor solubility of them than those of organic bases in toluene. Screening of solvent variety indicated that toluene is the best. The yields were much lower in the other solvents such as THF, CH_2Cl_2, acetone or 1,4-dioxane, even at higher refluxing temperature in xylene (Table S2, entries 8–13).

Secondly, the effects of catalyst loading and other parameters of reaction condition were examined. As seen in Table 1, if the catalyst loading increased from 1.0 mol% to 2.0 mol %, the yield of acetophenone was gradually improved from 84% to 91% (Table 1, entries 1–3). However, further increasing the catalyst loading to 3.0 mol% did not improve the yield (90%). Increasing the amounts of *t*-BuOK from 0.5 mmol to 2.0 mmol reduced the yield to 54% (entries 5–6 vs. 3). Different reaction temperatures were also tested. The reaction at a lower temperature (80 °C) afforded a much lower yield of 54% (entry 7). Shortening the reaction time by 2 hours (from 12 to 10 h) led to the yield decrease from 91% to 79% (entry 8 vs entry 3) and prolonging the reaction time to 24 did not improve the yield significantly (entry 9). The control experiments showed that only a small amount of acetophenone was obtained when the reaction was carried out in the absence of either a base or the Ru catalyst, suggesting both the two components play crucial role in the reaction (entries 10–11). Then, the catalytic activities of complexes **2**–**4** were investigated under the optimal conditions (entries 12–14). The yields indicated that the complexes **3** and **4** bearing electron-withdrawing substituents on the phenyl ring of the Schiff base ligand are a little more active than complex **2** bearing electron-rich substituent and **1** without any substituent. Finally, a poor yield was found when RuHCl(CO)(PPh₃)₃ was employed as the catalyst (entry 15).

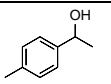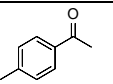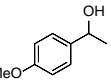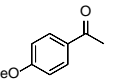**Table 1** Optimization of reaction conditions^a
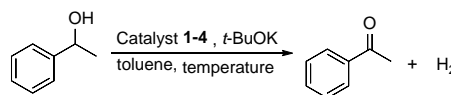
Entry	Catalyst (mol%)	Base/mmol	Temp./°C	Time/h	Yield^b/%
1	**1**(1.0)	0.5	110	12	84
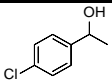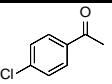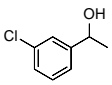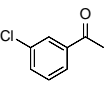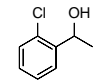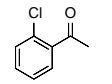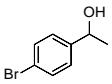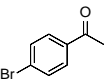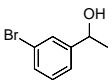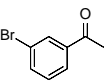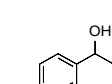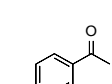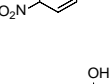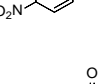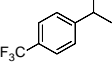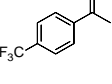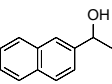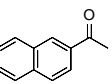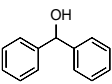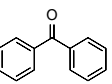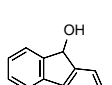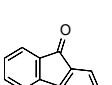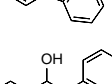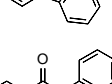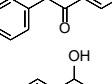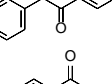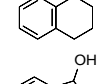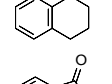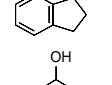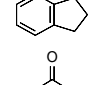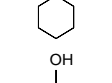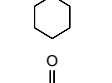
2	**1**(1.5)	0.5	110	12	87
3	**1**(2.0)	0.5	110	12	91
4	**1**(3.0)	0.5	110	12	90
5	**1**(2.0)	1.0	110	12	79
6	**1**(2.0)	2.0	110	12	54
7	**1**(2.0)	0.5	80	12	51
8	**1**(2.0)	0.5	110	10	79
9	**1**(2.0)	0.5	110	24	94
10	—	0.5	110	12	13
11	**1**(2.0)	—	110	12	25
12	**2**(2.0)	0.5	110	12	88
13	**3**(2.0)	0.5	110	12	94
14	**4**(2.0)	0.5	110	12	92
15	RuHCl(CO)(PPh₃)₃(2.0)	0.5	110	12	42

ᵃ Reaction conditions: 1-phenylethanol (1.0 mmol), toluene (4.0 mL) under N₂. *ᵇ* Determined by GC analysis.

Under the optimized conditions of Entry 13 in Table 1, we lastly examined the substrate generality of secondary alcohols for this catalytic system and the data are presented in Table 2. As shown, a variety of substituted 1-phenylethanols bearing electron-rich and electron-poor groups on the phenyl ring including 1-(naphthalen-2-yl)ethan-1-ol can be converted to the corresponding ketones in 88–94% yields (Table 2, entries 1–10). Notably, the potential steric hindrance by *o*-substituted group on 1-phenylethanol did not hamper the reaction. Reactions of diphenylmethanols were also proved to be amenable to afford the desired products in ~90% yields (entries 11–12). Likewise, benzoin was oxidized to give benzil in excellent yield (entry 13). The dehydrogenation reactions of benzocycloalkanols (1-tetralol and 1-indanol) were slightly low yielding under the typical condition. 1-Tetralone and 1-indanone were obtained in 85% and 82% yields respectively (entries 14–15). It is worth noting that aliphatic alcohols were also dehydrogenated very well by this catalytic system, generating the aliphatic ketones compounds in >80% yields (entries 16–18). Unsurprisingly, they reacted slower than the 1-phenylethanols and the reaction duration was prolonged by 12 more hours.

Table 2 Scope of secondary alcohols catalyzed by complex **3**ᵃ

Entry	Substrate	Product	Time/h	Yieldᵇ/%
1			12	89(84)
2			12	88(83)
3			12	92(89)
4			12	93(90)
5			12	90 (86)
6			12	94(92)
7			12	93(90)
8			12	91(84)
9			12	88(85)
10			12	91(86)
11			12	90(86)
12			12	90(85)
13			12	94(90)
14			12	85(80)
15			12	82(77)
16			24	87
17			24	85
18			24	82

ᵃ Reaction conditions: substrate (1.0 mmol), catalyst **3** (2.0 mol%), *t*-BuOK (0.5 mmol), toluene (4.0 mL) under N₂. *ᵇ* Determined by GC analysis. Isolated yields in the parentheses.
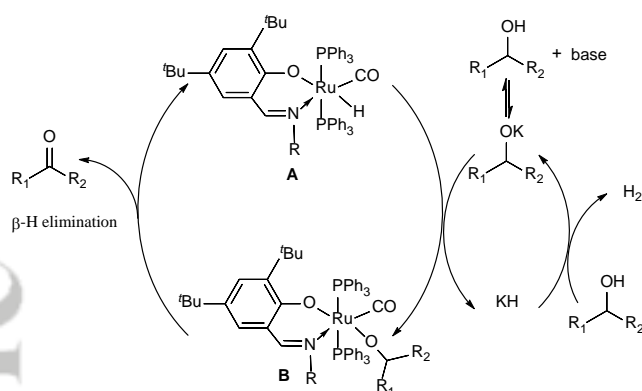
Scheme 2 Proposed catalytic cycle for the dehydrogenation of secondary alcohols.

Generally, the Ru-H core is regarded as the catalytically active species in transfer hydrogenation and dehydrogenation pathways.[22,35,36] Based on our experimental results and the literature reports,[24,37,38] a plausible mechanism was proposed in Scheme 2. First, the Ru complex **A** reacts with potassium alkoxide (from the alcohol and base) to give the RuII-alkoxide intermediate **B** and KH. Then **B** undergoes β-H elimination to afford the ketone product and regenerate **A**. Meanwhile, the KH formed in the first step reacts with the alcohol to release H_2 gas and produce potassium alkoxide to complete the catalytic cycle.

Conclusions

In summary, four ruthenium(II) complexes **1**—**4** bearing Schiff base ligand have been successfully synthesized and well characterized. All the complexes exhibit high catalytic activities for the acceptorless dehydrogenation of secondary alcohols to ketones. These catalysts are easy to synthesize from commercially available materials and are stable to air and moisture. Such a catalytic system operates under mild conditions and displays a broad functional group tolerance. It provides an alternative enviromentlly friendly approach to synthesize ketones.

Experimental

General considerations

All manipulations of potential air and moisture sensitive materials were performed under a dry argon atmosphere using standard Schlenk techniques. Solvents were distilled from appropriate drying agents under N_2 before use. 3,5-di-tert-butyl-2-hydroxybenzaldehyde, aniline, *p*-toluidine, *p*-chloroaniline, and 4-bromoaniline and other reagents were purchased from Boka Chemical Co. and used without further purification unless indicated. The Schiff base ligands were synthesized using literature method.[33] RuHCl(CO)(PPh₃)₃ was prepared according to the literature procedure.[34] ¹H and ³¹P{¹H} NMR spectra were recorded on a Zhongke-Niujin Quantum-I 400 spectrometer. Elemental analysis data were obtained on a Vario EL III element analyzer. IR spectra were recorded as KBr disks on a

Thermo Fisher iS 50 spectrometer. X-ray diffraction studies were carried out on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo-K□ radiation (λ = 0.71073 Å). Solution, refinement and geometrical calculations for all crystal structures were performed using SHELXTL.

Synthesis of complex 1

To a 50 mL of round-bottom flask was placed [RuHCl(CO)(PPh₃)₃] (0.81 g, 0.85 mmol) and 15 mL of anhydrous THF. The mixture was stirred at room temperature for half an hour. A solution of **L1** (0.26 g, 0.85 mmol) and triethylamine (1.05 g, 10.4 mmol) in 5 mL of anhydrous THF was then added and the resulting mixture was refluxed with stirring for 18 h. After being cooled to room temperature, the reaction was concentrated and the residue was purified by neutral Al_2O_3 chromatography to afford complex **1** as an orange solid (0.46 g, 57% yield). Single crystals suitable for X-ray crystallographic determination were grown from CH₂Cl₂/*n*-hexane solution at ambient temperature. Anal. Calc. for C₅₈H₅₇NO₂P₂Ru: C, 72.33; H, 5.97; N, 1.45. Found (%): C, 72.45; H, 5.82; N, 1.31. ¹H NMR (400 MHz, CDCl₃) δ: 7.48–7.44 (m, 13H, HC=N, Ar–H), 7.38 (s, 1H, Ar–H), 7.26–7.22 (m, 6H, Ar–H), 7.14 (t, 12H, *J* = 7.6 Hz, Ar–H), 7.02 (d, 2H, *J* = 7.6 Hz, Ar–H), 6.94 (s, 1H, Ar–H), 6.27 (d, 2H, *J* = 8.0 Hz, Ar–H), 6.23 (s, 1H, Ar–H), 1.18 (s, 9H, *t*Bu–H), 0.75 (s, 9H, *t*Bu–H), −10.41 (t, 1H, *J* = 19.7 Hz, Ru–H). ¹³C NMR (100 MHz, CDCl₃) δ: 205.6 (CO), 166.5 (HC=N), 165.4, 158.0, 134.5, 134.3, 132.7, 132.2, 132.1, 129.7, 129.2, 128.8, 128.6, 128.5, 128.2, 127.7, 127.5, 124.6, 123.5, 121.0, 34.8 (*C*Me₃), 33.50 (*C*Me₃), 31.4 (C*Me*₃), 29.5 (C*Me*₃). ³¹P{¹H} NMR (162 MHz, CDCl₃) δ: 40.9 (s, PPh₃). IR (KBr, cm⁻¹): 1914 (vs) ($v_{C≡O}$), 2006 (s) ($v_{Ru–H}$).

Synthesis of complex 2

Using the same procedure as described for **1**, with **L2** in place of **L1**, complex **2** was obtained as an orange solid (0.38 g, 46% yield). Anal. Calc. for C₅₉H₅₉NO₂P₂Ru: C, 72.52; H, 6.09; N, 1.43. Found (%): C, 72.64; H, 5.92; N, 1.55. ¹H NMR (400 MHz, CDCl₃) δ: 7.48–7.44 (m, 12H, HC=N, Ar–H), 7.34 (d, 3H, *J* = 10.4 Hz, Ar–H), 7.24–7.21 (m, 6H, Ar–H), 7.13 (t, 13H, *J* = 7.6 Hz, Ar–H), 6.92 (s, 1H, Ar–H), 6.83 (d, 2H, *J* = 8.0 Hz, Ar–H), 2.30 (s, 3H, CH₃), 1.17 (s, 9H, *t*Bu–H), 0.75 (s, 9H, *t*Bu–H), −10.39 (t, 1H, *J* = 19.6 Hz, Ru–H). ¹³C NMR (100 MHz, CDCl₃) δ: 205.7 (CO), 166.3 (HC=N), 165.2, 155.9, 141.6, 134.6, 134.4, 134.2, 132.6, 129.6, 129.2, 128.7, 127.7, 127.6, 123.3, 121.0, 34.9 (*C*Me₃), 33.50 (*C*Me₃), 31.5 (C*Me*₃), 29.6 (C*Me*₃), 20.8 (Ar*Me*). ³¹P{¹H} NMR (162 MHz, CDCl₃) δ: 40.9 (s, PPh₃). IR (KBr, cm⁻¹): 1916 (vs) ($v_{C≡O}$), 2041 (s) ($v_{Ru–H}$).

Synthesis of complex 3

Using the same procedure as described for **1**, with **L3** in place of **L1**, complex **3** was obtained as an orange solid (0.36 g, 42% yield). Anal. Calc. for C₅₈H₅₆ClNO₂P₂Ru: C, 69.83; H, 5.66; N, 1.40. Found (%): C, 69.68; H, 5.78; N, 1.25. ¹H NMR (400 MHz, CDCl₃) δ: 7.47–7.44 (m, 11H, HC=N, Ar–H), 7.25 (t, 7H, *J* = 6.8 Hz, Ar–H), 7.18–7.13 (m, 13H, Ar–H), 6.95 (d, 3H, *J* = 8.4 Hz, Ar–H), 6.25 (s, 1H, Ar–H), 6.13 (d, 2H, *J* = 8.4 Hz, Ar–H), 1.18 (s, 9H, *t*Bu–H), 0.73 (s, 9H, *t*Bu–H), −10.48 (t, 1H, *J* = 19.2 Hz, Ru–H). ¹³C NMR (100 MHz, CDCl₃) δ: 205.5 (CO), 166.5 (HC=N), 165.8, 156.5, 141.9, 134.5, 134.4, 133.0, 130.0. 129.5, 129.4, 129.3, 129.1, 128.0, 127.8 127.6, 124.7, 121.8, 34.8 (*C*Me₃), 33.50 (*C*Me₃), 31.4 (C*Me*₃),

29.4 (C*Me*₃). ³¹P{¹H} NMR (162 MHz, CDCl₃) δ: 41.0 (s, PPh₃). IR (KBr, cm⁻¹): 1916 (vs) ($v_{C=O}$), 2053 (s) (v_{Ru-H}).

Synthesis of complex 4

Using the same procedure as described for **1**, with **L4** in place of **L1**, complex **4** was obtained as an orange solid (0.39 g, 45% yield). Anal. Calc. for C₅₈H₅₆BrNO₂P₂Ru: C, 66.85; H, 5.42; N, 1.34. Found (%): C, 66.69; H, 5.56; N, 1.51. ¹H NMR (400 MHz, CDCl₃) δ: 7.47–7.43 (m, 12H, HC=N, Ar–H), 7.33 (s, 1H, Ar–H), 7.28–7.23 (m, 7H, Ar–H), 7.18–7.09 (m, 12H, Ar–H), 7.10 (d, 2H, *J* = 8.4 Hz, Ar–H), 6.94 (s, 1H, Ar–H), 6.07 (d, 2H, *J* = 8.4 Hz, Ar–H), 1.18 (s, 9H, ᵗBu–H), 0.72 (s, 9H, ᵗBu–H), –10.48 (t, 1H, *J* = 16.8 Hz, Ru–H). ¹³C NMR (100 MHz, CDCl₃) δ: 204.4 (CO), 166.3 (HC=N), 165.8, 156.8, 141.9, 134.9, 134.5, 134.4, 134.2, 133.0, 129.3, 127.8, 127.6, 125.1, 120.8, 117.8, 34.8 (C*Me*₃), 33.50 (C*Me*₃), 31.4 (C*Me*₃), 29.4 (C*Me*₃). ³¹P{¹H} NMR (162 MHz, CDCl₃) δ: 41.0 (s, PPh₃). IR (KBr, cm⁻¹): 1912 (vs) ($v_{C=O}$), 2052 (s) (v_{Ru-H}).

Typical procedure for acceptorless dehydrogenation of secondary alcohols

A mixture of 1-phenylethanol (1.0 mmol), catalyst (0.02mmol), *t*-BuOK (0.5 mmol) was stirred in toluene (4.0 mL) at 110 oC for 12 h under an N₂ atmosphere. After cooled to temperature, the reaction mixture was filtered through a plug of silica gel and analyzed by GC. Then the solvent was removed under reduced pressure. The resulting residue was purified by silica gel chromatography using petroleum ether/EtOAc as eluent to afford the desired product.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2018xxxxx.

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Entry for the Table of Contents

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N,O-Ru catalysts

$$R^1\text{—}CH(OH)\text{—}R^2 \longrightarrow R^1\text{—}C(O)\text{—}R^2 + H_2$$
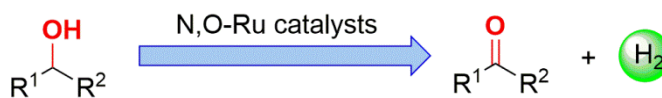
- easily accessed ligands
- stable catalyst
- good functional group compatibility
- high to excellent yields

Zhiqiang Hao,[a] Kang Liu,[a] Qi Feng,[a] Qing Dong,[a] Hongzhu Ma,*,[b] Zhangang Han,[a] Guo-Liang Lu,[c] and Jin Lin*,[a]

Four ruthenium(II) complexes **1—4** [RN=CH-(2,4-(^{t}Bu)$_2$C$_6$H$_2$O)]RuH(PPh$_3$)$_2$(CO) (R = C$_6$H$_5$, **1**; R = 4-MeC$_6$H$_4$, **2**; R = 4-ClC$_6$H$_4$, **3**; R = 4-BrC$_6$H$_4$, **4**) bearing Schiff base ligand were successfully synthesized. Their structures were fully characterized by elemental analysis, IR, NMR spectroscopy and X-ray crystallography. These Ru(II) complexes exhibit high catalytic performance and good functional-group compatibility in the acceptorless dehydrogenation of secondary alcohols, affording the corresponding ketones in 82—94% yields.