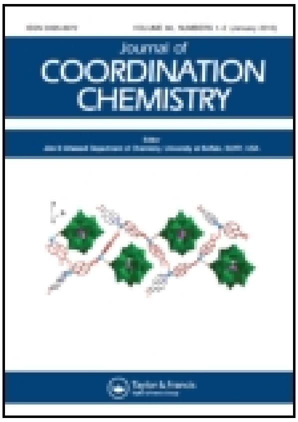
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:50
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis, structural characterization, and catalytic activity of ruthenium(II) monocarbonyl complexes with bidentate Schiff base and triphenylphosphine ligands

Xiao-Feng Yin[a], Hui Lin[ab], Ai-Quan Jia[b], Qun Chen[a] & Qian-Feng Zhang[ab]

[a] Department of Applied Chemistry, School of Petrochemical Engineering, Changzhou University, Jiangsu, P.R. China

[b] Institute of Molecular Engineering and Applied Chemistry, Anhui University of Technology, Ma'anshan, P.R. China

Accepted author version posted online: 05 Aug 2013.Published online: 24 Sep 2013.

To cite this article: Xiao-Feng Yin, Hui Lin, Ai-Quan Jia, Qun Chen & Qian-Feng Zhang (2013) Synthesis, structural characterization, and catalytic activity of ruthenium(II) monocarbonyl complexes with bidentate Schiff base and triphenylphosphine ligands, Journal of Coordination Chemistry, 66:18, 3229-3240, DOI: 10.1080/00958972.2013.831843

To link to this article: http://dx.doi.org/10.1080/00958972.2013.831843

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

Journal of Coordination Chemistry, 2013
Vol. 66, No. 18, 3229–3240, http://dx.doi.org/10.1080/00958972.2013.831843

Synthesis, structural characterization, and catalytic activity of ruthenium(II) monocarbonyl complexes with bidentate Schiff base and triphenylphosphine ligands

XIAO-FENG YIN†, HUI LIN†‡, AI-QUAN JIA‡, QUN CHEN† and
QIAN-FENG ZHANG*†‡

†Department of Applied Chemistry, School of Petrochemical Engineering, Changzhou University, Jiangsu, P.R. China
‡Institute of Molecular Engineering and Applied Chemistry, Anhui University of Technology, Ma'anshan, P.R. China

(*Received 5 March 2013; in final form 12 July 2013*)

Treatment of $[RuHCl(CO)(PPh_3)_3]$ with equal amounts of equiv. bidentate Schiff base 2[(4-chloro-phenylimino)-methyl]-phenol (HL-Cl) or 2(*p*-tolylimino-methyl)-phenol (HL-Me) or 2[(4-nitro-phenylimino)-methyl]-phenol ($HL-NO_2$) in the presence of triethylamine afforded $[RuCl(\kappa^2\text{-}N,O\text{-L-Cl})(CO)(PPh_3)_2]$ (**1**), $[RuCl(\kappa^2\text{-}N,O\text{-L-Me})(CO)(PPh_3)_2]$ (**2**), and $[RuCl(\kappa^2\text{-}N,O\text{-L-NO}_2)(CO)(PPh_3)_2]$ (**3**), respectively. The molecular structures of **1**, **2**, and **3**$\cdot 1.5C_6H_{14}$ have been determined by single-crystal X-ray crystallography. Complexes **1–3** were used for oxidation of primary and secondary alcohols to aldehydes and ketones as catalysts in the presence of *N*-methylmorpholine-*N*-oxide.

Keywords: Ruthenium; Schiff base; Synthesis; Crystal structure; Catalytic property

1. Introduction

Ruthenium Schiff base complexes have been found to be catalytically active for various organic transformations such as cyclopropanation, ring opening of epoxides, oxidation of sulfides, aziridination, the Diels–Alder reaction, and epoxidation of olefins [1, 2, 4, 5]. Ruthenium complexes containing tri- and tetradentate Schiff bases have been well studied [6–9], whereas, those with bidentate Schiff base ligands have received comparatively less attention [10]. There has been an increasing interest during recent years in ruthenium complexes with bidentate ligands containing π-acceptor and σ-donor groups [10, 12]. The *N*,*O*-donor Schiff bases in this study have been prepared from salicylaldehyde and substituted phenylamines [13]. These Schiff bases bond bidentate to the ruthenium(II) center which forced the aryl rings of the Schiff base into a conformation, leading to an approximately coplanar six-membered ring with the basal plane of octahedral ruthenium(II) [10, 12, 14]. Ruthenium triphenylphosphine and ruthenium carbonyl complexes containing

---

*Corresaponding author. Email: zhangqf@ahut.edu.cn

Schiff base have shown good activity and selectivity in oxidation and sulfimidation processes, respectively [5, 15–17]. Hence, we synthesize a series of ruthenium(II) complexes with *N*,*O*-bidentate Schiff base ligands and study their reactivity. Selective and efficient catalysts have been reported, such as ruthenium(II) carbonyl complexes with *N*-[di(alkyl/aryl)carbamothioyl]benzamide derivatives reported by Karvembu [18], copper(II)-azo complexes by Shoair [19], multi-walled carbon nanotube-bound nickel Schiff base complexes by Bhat [20], chromium(VI) complexes by Saha [21], inorganic/organic hybrid catalyst based on zinc-substituted polyoxometalate, ionic liquid by Mirkhani, Yadollahi, and Moghadam [22], and vanadium(IV) Schiff base complexes by Bagherzadeh [23], for oxidation of alcohols to aldehydes or ketones in the presence of different oxidants including NMO [18], H_2O_2 [19, 22], periodic acid H_5IO_6, [20] and oxone [23]. Herein, we report the synthesis, structural characterization, and catalytic activity of ruthenium(II) monocarbonyl complexes with *N*,*O*-bidentate Schiff base and triphenylphosphine.

2. Experimental

2.1. *General*

All synthetic manipulations were carried out under dry nitrogen by standard Schlenk techniques. Salicylaldehyde, 4-chloro-phenylamine, 4-methyl-phenylamine, and 4-nitro-

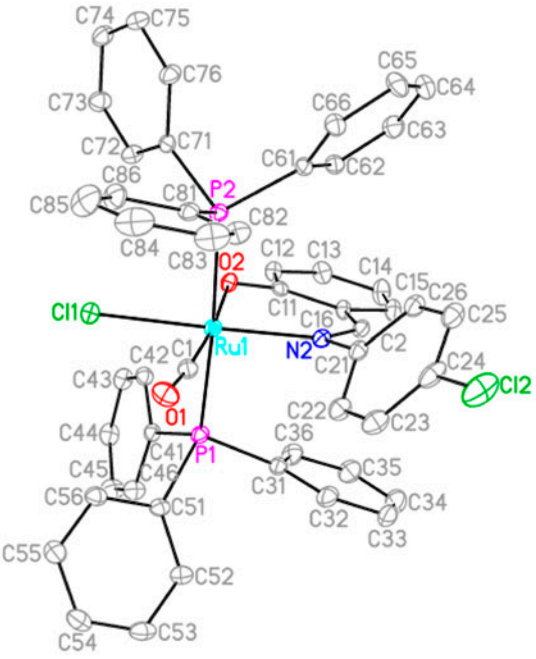


Figure 1. Molecular structure of [RuCl(κ^2-*N,O*-L-Cl)(CO)(PPh_3)$_2$] (**1**). Selected bond lengths (Å) and angles (°): Ru(1)–C(1) 1.831(4), Ru(1)–O(2) 2.078(2), Ru(1)–N(2) 2.114(3), Ru(1)–P(2) 2.4098(9), Ru(1)–P(1) 2.4230(9), Ru(1)–Cl(1) 2.4294(10); C(1)–Ru(1)–O(2) 174.12(13), C(1)–Ru(1)–N(2) 98.28(14), O(2)–Ru(1)–N(2) 87.49(10), C(1)–Ru(1)–P(2) 90.50(11), O(2)–Ru(1)–P(2) 88.36(7), N(2)–Ru(1)–P(2) 90.25(8), P(2)–Ru(1)–P(1) 175.01(3), C(1)–Ru(1)–Cl(1) 84.90(12), O(2)–Ru(1)–Cl(1) 89.32(7), N(2)–Ru(1)–Cl(1) 176.82(9).

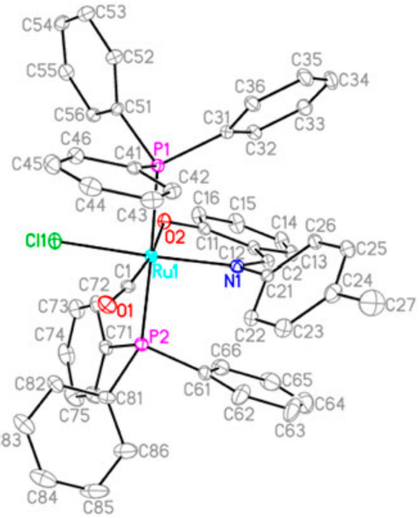


Figure 2. Molecular structure of [RuCl(κ^2-*N,O*-L-Me)(CO)(PPh_3)$_2$] (**2**). Selected bond lengths (Å) and angles (°): Ru(1)–C(1) 1.835(4), Ru(1)–O(2) 2.087(2), Ru(1)–N(1) 2.111(3), Ru(1)–P(1) 2.4054(9), Ru(1)–P(2) 2.4184(9), Ru (1)–Cl(1) 2.4245(9); C(1)–Ru(1)–O(2) 171.72(12), C(1)–Ru(1)–N(1) 99.90(13), O(2)–Ru(1)–N(1) 88.19(10), C(1)–Ru(1)–P(1) 88.57(10), O(2)–Ru(1)–P(1) 89.64(6), N(1)–Ru(1)–P(1) 89.98(7), P(1)–Ru(1)–P(2) 177.40(3), C(1)–Ru (1)–Cl(1) 85.18(10), O(2)–Ru(1)–Cl(1) 86.72(6),N(1)–Ru(1)–Cl(1) 174.91(8), P(1)–Ru(1)–Cl(1) 89.77(3).

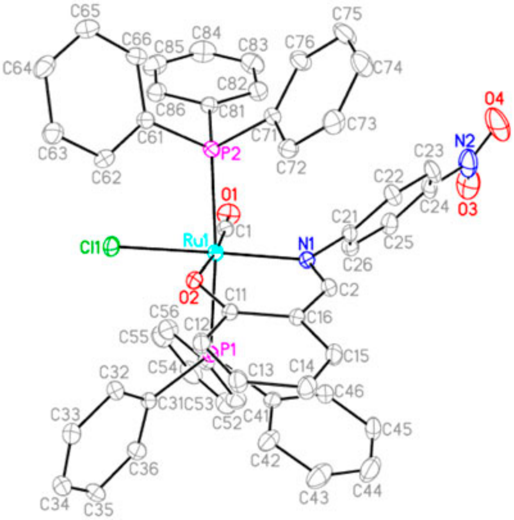


Figure 3. Molecular structure of [RuCl(κ^2-*N,O*-L-NO_2)(CO)(PPh_3)$_2$] (**3**). Selected bond lengths (Å) and angles (°): Ru(1)–C(1) 1.846(5), Ru(1)–O(2) 2.086(3), Ru(1)–N(1) 2.113(3), Ru(1)–P(2) 2.4073(11), Ru(1)–P(1) 2.4243 (11), Ru(1)–Cl(1) 2.4262(11); C(1)–Ru(1)–O(2) 174.60(15), C(1)–Ru(1)–N(1) 97.29(16), O(2)–Ru(1)–N(1) 87.94 (11), C(1)–Ru(1)–P(2) 89.28(13), O(2)–Ru(1)–P(2) 89.17(8), N(1)–Ru(1)–P(2) 92.14(9), P(2)–Ru(1)–P(1) 175.03 (4), C(1)–Ru(1)–Cl(1) 86.41(14), O(2)–Ru(1)–Cl(1) 88.36(8), N(1)–Ru(1)–Cl(1) 176.30(10), P(2)–Ru(1)–Cl(1) 87.75(4).

phenylamine were purchased from Alfa Aesar Ltd. and used without purification. [RuHCl(CO)(PPh_3)$_3$] was prepared according to the literature method [24]. NMR spectra were recorded on a Bruker ALX 400 Plus spectrometer operating at 400 and 162 MHz for ^1H and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^1H) and H_3PO_4 (^{31}P). Electronic absorption spectra were obtained on a Shimadzu UV-3000 spectrophotometer. Infrared spectra (KBr) were recorded on a Perkin–Elmer 16 PC FT-IR spectrophotometer with the use of pressed KBr pellets and the positive FAB mass spectra were recorded on a Finnigan TSQ 7000 spectrometer. Elemental analyzes were carried out using a Perkin–Elmer 2400 CHN analyzer.

2.2. *Synthesis and characterization*

2.2.1. General procedure for preparation of Schiff base ligands (HL). A methanol (25 mL) solution of salicylaldehyde (15 mM) was added to substituted aniline (15 mM) in a round-bottomed flask equipped with a condenser. The reaction mixture was stirred at reflux for 24 h. After completion of reaction, the yellow crystalline product precipitated upon cooling. The solid product was filtered, washed with cold methanol, and dried in air.

2.2.2. 4-Chloro-phenylsalicylaldimine (HL-Cl). Yellow solid, yield: 96%; IR (KBr disk, cm^{-1}): 3574 ($\nu_{O\text{–}H}$), 1635 ($\nu_{C=N}$), 769 ($\nu_{C\text{–}Cl}$); ^1H NMR ($CDCl_3$, 400 MHz): δ 6.97–7.14 (m, 6H, Ar*H*), 7.45 (d, 2H, $J = 5.7$ Hz, Ar*H*), 8.26 (s, 1H, –C*H*=N), 12.75 (s, 1H, O*H*) ppm; MS (FAB): *m*/*z* 231 [M^+], 196 [M^+–Cl]. Anal. Calcd for $C_{13}H_9NOCl$ (%): C, 67.69; H, 3.93; N, 6.07. Found: C, 67.62; H, 3.91; N, 6.03.

2.2.3. 4-Methyl-phenylsalicylaldimine (HL-Me). Yellow solid, yield: 93%; IR (KBr disk, cm^{-1}): 3586 ($\nu_{O\text{–}H}$), 1639 ($\nu_{C=N}$); ^1H NMR ($CDCl_3$, 400 MHz): δ 2.23 (s, 3H, C*H*$_3$), 7.02–7.19 (m, 6H, Ar*H*), 7.36 (d, 2H, $J = 6.2$ Hz, Ar*H*), 8.37 (s, 1H, –C*H*=N), 12.94 (s, 1H, O*H*) ppm; MS (FAB): *m*/*z* 210 [M^+]. Anal. Calcd for $C_{14}H_{12}NO$ (%): C, 79.98; H, 5.75; N, 6.66. Found: C, 79.70; H, 5.73; N, 6.61.

2.2.4. 4-Nitro-phenylsalicylaldimine (HL-NO_2). Yellow solid, yield: 94%; IR (KBr disk, cm^{-1}): 3596 ($\nu_{O\text{–}H}$), 1642 ($\nu_{C=N}$), 1572, 1369 (ν_{NO2}); ^1H NMR ($CDCl_3$, 400 MHz): δ 6.93–7.27 (m, 6H, Ar*H*), 7.58 (d, 2H, $J = 6.4$ Hz, Ar*H*), 8.71 (s, 1H, –C*H*=N), 13.02 (s, 1H, O*H*) ppm; MS (FAB): *m*/*z* 241 [M^+], 195 [M^+–NO_2]. Anal. Calcd for $C_{13}H_9N_2O_3$ (%): C, 64.73; H, 3.76; N, 11.61. Found: C, 64.45; H, 3.73; N, 11.57.

2.2.5. General procedure for preparation of ruthenium complexes 1–3. To a round-bottomed flask with a stir bar was placed [RuHCl(CO)(PPh_3)$_3$] (0.81 g, 0.85 mM) under nitrogen. Pre-dried THF (10 mL) was added and the resulting mixture was stirred at room temperature. Then, ligand (0.85 mM) and excess triethylamine (1.05 g, 10.4 mM) in THF (5 mL) were added. The reaction mixture was stirred at room temperature overnight. After removal of solvents, dichloromethane (20 mL) was added and the solution was filtered. The filtrate was concentrated and the residue was washed with diethyl ether (5 mL × 2) and hexane (5 mL × 2) to give the desired product. Recrystallization from CH_2Cl_2/hexane (1 : 1) afforded yellow needle crystals in two days suitable for X-ray diffraction.

2.2.6. [RuCl(κ^2-N,O-L-Cl)(CO)(PPh_3)$_2$] (1). Yield: 0.44 g, 56%. IR (KBr disk, cm^{-1}): 1909 ($\nu_{C\equiv O}$), 1621 ($\nu_{C=N}$); ^{31}P NMR (C*D*Cl_3, 400 MHz): δ 22.1 (s, PPh_3) ppm. ^{1}H NMR (C*D*Cl_3, 400 MHz): δ 6.91–7.18 (m, 36H, Ar*H*), 7.47 (d, 2H, *J* = 5.9 Hz, Ar*H*), 8.35 (s, 1H, –C*H*=*N*) ppm. MS (FAB): *m*/*z* 919 [M^+], 891 [M^+–CO], 884 [M^+–Cl], 856 [Ru(κ^2-*N*,*O*-L-Cl)(PPh_3)$_2$]$^+$, 594 [Ru(κ^2-*N*,*O*-L-Cl)(PPh_3)]$^+$, 332 [Ru(κ^2-*N*,*O*-L-Cl)]$^+$. Anal. Calcd for $C_{50}H_{39}NO_2Cl_2P_2Ru$ (%): C, 65.29; H, 4.27; N, 1.52. Found: C, 65.14; H, 4.23; N, 1.56.

2.2.7. [RuCl(κ^2-N,O-L-Me)(CO)(PPh_3)$_2$] (2). Yield: 0.36 g, 47%. IR (KBr disk, cm^{-1}): 1914 ($\nu_{C\equiv O}$), 1627 ($\nu_{C=N}$); ^{31}P NMR (C*D*Cl_3, 400 MHz): δ 21.6 (s, PPh_3) ppm. ^{1}H NMR (C*D*Cl_3, 400 MHz): δ 2.26 (s, 3H, C*H*$_3$), 6.98–7.23 (m, 36H, Ar*H*), 7.41 (d, 2H, *J* = 5.9 Hz, Ar*H*), 8.49 (s, 1H, –C*H*=N) ppm. MS (FAB): *m*/*z* 899 [M^+], 871 [M^+–CO], 864 [M^+–Cl], 836 [Ru(κ^2-*N*,*O*-L-Cl)(PPh_3)$_2$]$^+$, 574 [Ru(κ^2-*N*,*O*-L-Cl)(PPh_3)]$^+$, 312 [Ru(κ^2-*N*,*O*-L-Cl)]$^+$. Anal. Calcd for $C_{51}H_{42}NO_2Cl$–P_2Ru (%): C, 68.11; H, 4.71; N, 1.56. Found: C, 68.03; H, 4.65; N, 1.52.

2.2.8. [RuCl(κ^2-N,O-L-NO_2)(CO)(PPh_3)$_2$] 1.5C_6H_{14} (3·1.5C_6H_{14}). Yield: 0.35 g, 42%. IR (KBr disk, cm^{-1}): 1912 ($\nu_{C\equiv O}$), 1630 ($\nu_{C=N}$), 1587, 1373 (ν_{NO2}); ^{31}P NMR (C*D*Cl_3, 400 MHz): δ 22.9 (s, PPh_3) ppm. ^{1}H NMR (C*D*Cl_3, 400 MHz): δ 6.93–7.36 (m, 36H, Ar*H*), 7.49 (d, 2H, *J* = 5.9 Hz, Ar*H*), 8.53 (s, 1H, –C*H*=N) ppm. MS (FAB): *m*/*z* 858 [M^+], 830 [M^+–CO], 823 [M^+–Cl], 795 [Ru(κ^2-*N*,*O*-L-NO_2)(PPh_3)$_2$]$^+$, 533 [Ru(κ^2-*N*,*O*-L-NO_2)(PPh_3)]$^+$, 271 [Ru(κ^2-*N*,*O*-L-NO_2)]$^+$. Anal. Calcd for $C_{44}H_{39}N_2O_4ClP_2Ru\cdot{}^3/_2(C_6H_{14})$ (%): C, 64.46; H, 6.12; N, 2.84. Found: C, 64.27; H, 6.06; N, 2.79.

2.3. *X-ray crystallography*

A summary of crystallographic data and experimental details for **1**, **2**, and **3**·1.5C_6H_{14} is summarized in table 1. Intensity data were collected on a Bruker SMART APEX 2000 CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 296(2) K. The collected frames were processed with SAINT [25]. The data were corrected for absorption using SADABS [26]. Structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [28]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogens were generated geometrically (C_{sp3}–H = 0.96 and C_{sp2}–H = 0.93 Å) and included in the structure factor calculations with assigned isotropic thermal parameters but were not refined. The hexane molecules in **3**·1.5C_6H_{14} were isotropically refined without hydrogens due to disorder, which probably resulted in a relatively high *R* value in the final refinement.

2.4. *Procedure for catalytic oxidation of alcohols*

Oxidation of primary alcohols to aldehydes and secondary ones to ketones with NMO were catalyzed in the presence of [RuCl(κ^2-*N*,*O*-L-Cl)(CO)(PPh_3)$_2$] (**1**), [RuCl(κ^2-*N*,*O*-L-Me)(CO)(PPh_3)$_2$] (**2**), or [RuCl(κ^2-*N*,*O*-L-NO_2)(CO)(PPh_3)$_2$] (**3**). A typical reaction using **1**, **2**

Table 1. Crystallographic data and experimental details for **1**, **2,** and **3**$\cdot 1.5C_6H_{14}$.

Complex	**1**	**2**	**3**$\cdot 1.5C_6H_{14}$
Empirical formula	$C_{50}H_{39}NO_2Cl_2P_2Ru$	$C_{51}H_{42}NO_2ClP_2Ru$	$C_{53}H_{60}N_2O_4ClP_2Ru$
Formula weight	919.73	899.32	987.49
Crystal system	Monoclinic	Triclinic	Triclinic
a (Å)	36.4797(11)	9.0870(2)	9.0619(4)
b (Å)	9.1618(3)	10.2937(2)	12.7710(5)
c (Å)	24.8066(7)	23.4627(5)	20.3154(9)
α (°)		96.328(1)	80.336(3)
β (°)	97.445(2)	94.825(1)	89.068(3)
γ °)		97.454(1)	89.575(3)
V (Å^3)	8221.0(4)	2152.06(8)	2303.16(17)
Space group	*C2/c*	*P-1*	*P-1*
Z	8	2	2
D_{Calc} (g cm^{-3})	1.486	1.388	1.424
Temperature (K)	296(2)	296(2)	296(2)
F (000)	3760	924	1030
μ(Mo-Kα) (mm^{-1})	0.633	0.542	0.517
Total refln.	39,275	27,123	31,934
Independent refln.	9352	8417	10,593
Parameters	523	524	565
R_{int}	0.0907	0.0657	0.0574
R_1[a], wR_2[b] ($I > 2\sigma(I)$)	0.0490, 0.0830	0.0437, 0.0847	0.0554, 0.1257
R_1, wR_2 (all data)	0.0641, 0.1009	0.0724, 0.0959	0.0755, 0.1511
GoF[c]	0.981	1.031	0.933

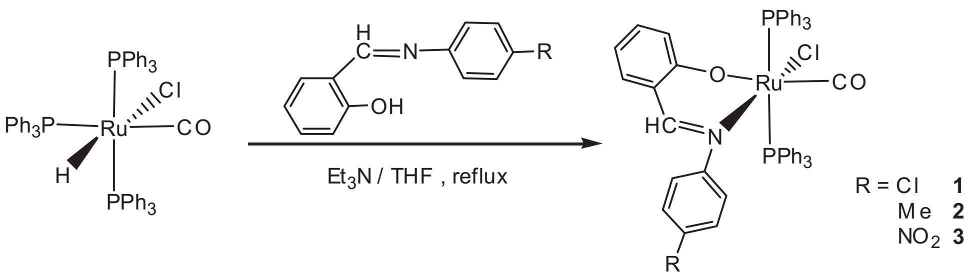
[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.
[c] $\text{GoF} = [\Sigma w(|F_o| - |F_c|)^2/(N_{\text{obs}} - N_{\text{param}})]^{1/2}$.

or **3** as catalyst is as follows. A solution of **1**, **2** or **3** (1 M%) in 20 mL of CH_2Cl_2 was added to the mixture of substrate (1 mM) and NMO (2 mM). The mixture was stirred at room temperature for 9 h and the solvent was evaporated under reduced pressure with a rotary evaporator resulting in a solid mass. It was shaken with petroleum ether (30–40 °C) (20 mL). The oxidized product extracted into petroleum ether was analyzed by GC.

3. Results and discussion

2[(4-chloro-phenylimino)-methyl]-phenol (HL-Cl), 2(*p*-tolyimino-methyl)-phenol (HL-Me), and 2[(4-nitro-phenylimino)-methyl]-phenol (HL-NO_2) were easily prepared by condensation of salicylaldehyde with the appropriate substituted aniline in methanol. Interactions of [RuHCl(CO)(PPh_3)$_3$] with HL-Cl, HL-Me and HL-NO_2 at room temperature in THF in the presence of organic base afforded [RuCl(κ^2-*N*,*O*-L-Cl)(CO)(PPh_3)$_2$] (**1**), [RuCl(κ^2-*N*,*O*-L-Me)(CO)(PPh_3)$_2$] (**2**), and [RuCl(κ^2-*N*,*O*-L-NO_2)(CO)(PPh_3)$_2$] (**3**) in 56, 47, and 42% yields, repectively, as shown in scheme 1. One PPh_3 and the hydride in the starting ruthenium hydride compound were replaced by one bidentate *O*,*N*-ligand.

The electronic spectra of **1–3** in dichloromethane showed three bands from 245 to 500 nm (see Supplementary material). The high intensity bands at 257 nm have been assigned to intraligand transitions [29]. The low energy absorptions at 348 nm are due to charge transfer transitions arising from the metal t_{2g} level to the unfilled π^* molecular orbital of the

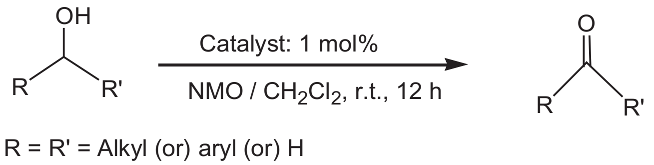


Scheme 1. Syntheses of ruthenium(II) monocarbonyl complexes with bidentate *O,N*-ligands.

ligand. The bands from 435 to 462 nm have been assigned to spin-allowed metal-ligand charge transition and d→d transitions. The nature of electronic spectra is similar to those observed for other octahedral ruthenium(II)-carbonyl triphenylphosphine complexes [30–33]. IR spectra of HL-Cl, HL-Me, and HL-NO_2 showed the CH=N at 1635, 1639, and 1642 cm^{-1}, respectively. In their corresponding ruthenium complexes, the blue bandshifted about 13 cm^{-1} (**1**, 1621 cm^{-1}; **2**, 1627 cm^{-1}, **3** 1630 cm^{-1}), suggesting coordination of nitrogen to ruthenium. The phenolic O–H of HL (3574–3596 cm^{-1}) could no longer be observed in IR spectra of **1–3**, presenting coordination of oxygen to ruthenium. The stretches of terminal C≡O in **1–3** were found from 1909 to 1914 cm^{-1}, comparable to ruthenium carbonyl complexes with *NOS* Schiff base and triphenylphosphine (1919–1933 cm^{-1}) [31]. Only one ^{31}P signal was observed in the ^{31}P NMR spectra of **1** (22.1 ppm), **2** (21.6 ppm), and **3** (22.9 ppm) due to *trans* PPh_3 ligands. The aldimine proton (–C*H*=N–) resonances of **1** ($\delta = 8.35$ ppm), **2** ($\delta = 8.49$ ppm), and **3** ($\delta = 8.53$ ppm) shift downfield compared to the free ligands HL-Cl ($\delta = 8.26$ ppm), HL-Me ($\delta = 8.37$ ppm), and HL-NO_2 ($\delta = 8.71$ ppm), suggesting coordination of nitrogen to ruthenium. The positive ion FAB mass spectra of **1–3** display the expected peaks corresponding to the molecular ions {[M^+], [M^+–Cl] or [M^+–CO], and $[ML(PPh_3)_2]^+$, $[ML(PPh_3)]^+$ or $[ML]^+$} with the characteristic isotopic distribution patterns.

The structures of **1**, **2**, and **3**$\cdot 1.5C_6H_{14}$ have been established by X-ray crystallography. Perspective views of the molecular structures of **1–3** are shown in figures 1–3, respectively. The central ruthenium is bonded in a slightly distorted octahedral geometry, to a nitrogen, a oxygen of the Schiff base, a carbon monoxide, two triphenylphosphines, and a terminal chloride. The Schiff base is bidentate to ruthenium and forms a six-membered chelate ring with O–Ru–N bite angles of 87.49(10)°, 88.19(10)° and 87.94(11)° for **1**, **2**, and **3**$\cdot 1.5C_6H_{14}$, respectively. The *trans* P–Ru–P angles are 175.01(3)°, 177.40(3)°and 175.03 (4)° for **1**, **2**, and **3**$\cdot 1.5C_6H_{14}$, respectively. The Ru–C bond lengths (1.831(4) Å in **1**, 1.835 (4) Å in **2,** and 1.846(5) Å in **3**$\cdot 1.5C_6H_{14}$) and the Ru–C–O bond angles (174.8(4)° in **1**, 173.5(3)° in **2,** and 176.3(4)° in **3**$\cdot 1.5C_6H_{14}$) are normal for ruthenium-carbonyl complexes [30–34]. The average Ru–P lengths are 2.4164(9), 2.4119(9), and 2.4158(11) Å for **1**, **2**, and **3**$\cdot 1.5C_6H_{14}$, respectively, and the average Ru–Cl lengths are 2.4294(10), 2.4245(9), and 2.4262(11) Å for **1**, **2**, and **3**$\cdot 1.5C_6H_{14}$, respectively, in agreement with those in related ruthenium(II) complexes [30–35].

Complexes **1–3** catalyze oxidation of primary alcohols to the corresponding aldehydes and secondary alcohols to ketones in dichloromethane in the presence of *N*-methylmorpholine-*N*-oxide (NMO) (scheme 2). Karvembu reported a catalytic system: $[Ru(L)(CO)(PPh_3)_2]$/NMO/DCM (L = binegative tridentate ONS Schiff base;

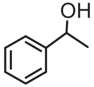
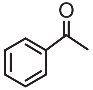
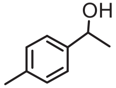
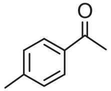
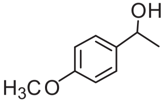
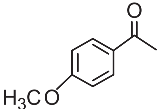
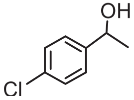
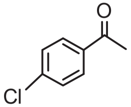
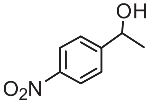
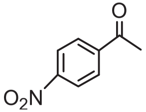
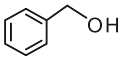
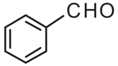
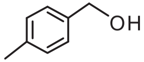
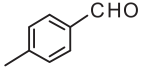


Scheme 2. Catalytic oxidation reactions of alcohols to aldehydes/ketones.

NMO, 3 mM; DCM = dichloromethane), for oxidation of alcohols to carbonyl compounds, and stated that neither the Ru complex nor the NMO alone causes the organic transformation under defined conditions [31]. In our catalytic system, dichloromethane is also the best solvent and the Ru catalyst amount is 1 M%, but 2 mM of NMO instead of 3 mM is enough for the catalysis. A series of alcohols, including benzylic alcohol with different substituents, benzylic secondary alcohols with different substituents, cyclohexanol, and 1-cyclohexyl-ethanol, have been chosen as substrates. [RuHCl(CO)(PPh$_3$)$_3$] showed less catalysis than **1–3**, exhibiting 64% conversion of benzylic alcohol into benzaldehyde, whereas **1–3** showed approximately 95% transformation under the same conditions. The oxidation products were identified by GC. The TON (%conversion) values are given in table 2 and indicate that the present ruthenium(II) complexes are promising catalysts. All substrates were efficiently converted to the corresponding ketones or aldehydes. Benzylic alcohol and substituted benzylic alcohols (entries 6–10) bearing either electron-donating or electron-withdrawing groups afforded the corresponding aldehydes in good conversions (93–99%), similar to previously reported Ru(II)-PPh$_3$/NMO catalytic systems with tridentate *ONS* Schiff base ligands (97–99%) [31] and Ru(II)-PPh$_3$/NMO catalytic systems with *N*-[di (alkyl/aryl)carbamothioyl] benzamide derivatives (94%) [18]. The efficiency of oxidation of benzylic alcohols is higher than that reported for Ru(II)-PPh$_3$ catalytic systems with bi- or tridentate ONO Schiff base (70%) [36] and [Ru(PPh$_3$)$_3$Cl$_2$]/hydroquinone/air systems (80%) [37].

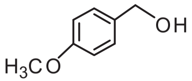
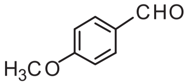
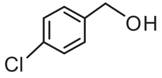
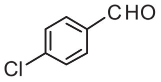
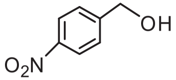
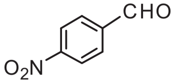
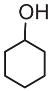
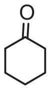
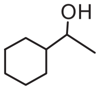
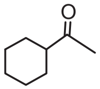
Benzylic secondary alcohols were smoothly oxidized to the corresponding ketones with good yields (82–93%), comparable to the observed ruthenium complexes containing *N*-[di(alkyl/aryl)carbamothioyl]-benzamide and triphenylphosphine ligands (94–99%) [18], but the catalytic activity was lower than the tetrametallic ruthenium-μ-oxo-μ-hydroxo catalyst (100%) [38] and heterogeneous nickel catalysts with Schiff base ligands (about 95%) [20]. No further oxidation of aldehydes to acids was observed even after extended reaction time, indicating good selectivity of **1–3**. Unlike benzylic alcohols and benzylic secondary alcohols, the conversion was not encouraging for cyclohexanol and 1-cyclohexylethanol which were converted into their corresponding ketones in 74–82% yields, similar to ruthenium complexes with tridentate *ONS* Schiff base ligands (68–80%) [31], but slightly higher than that in Ru(II)-PPh$_3$ catalytic systems with bi or tri-dentate *ONO* Schiff bases (42–85%) [36]. The catalytic oxidation activities of the present three ruthenium(II)-monocarbonyl complexes are not affected by the different electron-donating and electron-withdrawing *N*,*O*-bidentate Schiff bases. Investigations to understand catalytic mechanisms and properties of the ruthenium(II) complexes containing bidentate and tridentate Schiff base ligands are in progress.

Table 2. Oxidation of alcohols to corresponding aldehydes and ketones with NMO catalyzed by **1**, **2,** and **3**.[a]

			TON (% conversion)[b]		
Entry	Substrates	Products	**1**	**2**	**3**[a]
1			2.23×10^3 (86)	1.83×10^3 (89)	2.17×10^3 (82)
2			2.26×10^3 (89)	1.95×10^3 (83)	2.01×10^3 (83)
3			2.52×10^3 (84)	2.09×10^3 (87)	2.04×10^3 (81)
4			2.03×10^3 (91)	1.87×10^3 (93)	2.25×10^3 (90)
5			1.91×10^3 (93)	1.74×10^3 (90)	2.10×10^3 (91)
6			3.19×10^3 (95)	2.19×10^3 (94)	3.11×10^3 (96)
7			3.12×10^3 (96)	2.31×10^3 (97)	3.18×10^3 (98)

(*Continued*)

Table 2. (*Continued*).

			TON (% conversion)[b]		
Entry	Substrates	Products	**1**	**2**	**3**[a]
8			3.24×10^3 (93)	2.42×10^3 (94)	3.07×10^3 (97)
9			3.15×10^3 (98)	2.01×10^3 (97)	3.04×10^3 (99)
10			2.99×10^3 (94)	2.07×10^3 (95)	2.49×10^3 (93)
11			2.23×10^3 (80)	1.83×10^3 (81)	2.17×10^3 (82)
12			1.02×10^3 (81)	7.92×10^2 (78)	9.45×10^2 (74)

[a] Reaction conditions: alcohol (1 mmol), NMO (2 mmol), catalyst (0.01 mmol), dichloromethane (20 mL), stirring for 12 h, room temperature.
[b] Yield is determined by GC with area normalization.

4. Conclusion

Three new ruthenium(II) monocarbonyl complexes with bidentate Schiff base and triphenylphosphines have been synthesized and characterized by microanalytical and spectroscopic methods. Their molecular structures have been determined by single-crystal X-ray crystallography. The ruthenium complexes exhibit excellent catalytic performance on oxidation of alcohols to corresponding aldehydes or ketones in the presence of NMO, and the Schiff base ligands with different electron-donating and electron-withdrawing groups have little influence on the catalytic activity. It may provide a simple and alternative method for the oxidation of different kinds of alcohols under mild conditions.

Supplementary material

Crystallographic data for **1**, **2**, and **3**$\cdot 1.5C_6H_{14}$ have been deposited with the Cambridge Crystallographic Data Center as Supplementary publication Nos CCDC 925317–925319, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (+44) 1233 336 033; Email: deposit@ccdc.cam.ac.uk].

Acknowledgment

This project was supported by the Natural Science Foundation of China (20771003 and 21201003).

References

[1] L. Cannli, D.C. Sherrington. *Chem. Soc. Rev.,* **28**, 85 (1999) and reference therein.
[2] G.Y. Li, J. Zhang, P.W.H. Chan, X.J. Xu, N. Zhu, C.M. Che. *Organometallics*, **25**, 1676 (2006).
[3] K. Nakata, T. Takeda, J. Mihara, R. Irie, T. Katsuki. *Chem.–Eur. J.,* **7**, 3776 (2001).
[4] H. Kawabata, K. Omura, T. Uchida, T. Katsuki. *Chem. Asian J.*, **2**, 248 (2007).
[5] Y. Tamura, T. Uchida, T. Katsuki. *Tetrahedron Lett.*, **44**, 3301 (2003).
[6] C.-M. Che, J.-S. Huang. *Coord. Chem. Rev.*, **242**, 97 (2003).
[7] R. Irie, T. Katsuki. *Chem. Rev.*, **4**, 96 (2004).
[8] W.-L. Man, H.-K. Kwong, W.W.Y. Lam, J. Xiang, T.-W. Wong, W.-H. Lam, W.-T. Wong, S.-M. Peng, T.-C. Lau. *Inorg. Chem.*, **47**, 5936 (2008).
[9] P. Pattanayak, D. Patra, J.L. Pratihar, A. Burrows, M.F. Mahon, S. Chattopadhyay. *Inorg. Chim. Acta*, **363**, 2865 (2010).
[10] J.D.E.T. Wilton-Ely, M. Wang, S.J. Honarkhah, D.A. Tocher. *Inorg. Chim. Acta*, **358**, 3218 (2005).
[11] A.K. Das, S.-M. Peng, S. Bhattacharyya. *J. Chem. Soc., Dalton Trans.,* 181 (2000).
[12] K. Hiraki, Y. Kinoshita, H. Ushiroda, S. Koyama, H. Kawano. *Chem. Lett.*, 1243 (1997).
[13] A.I. Vogel. *A Text Book of Practical Organic Chemistry*, pp. 957–958, ELBS, London (1997).
[14] P. Bhattacharyya, M.L. Loza, J. Parr, A.M.Z. Slawin. *J. Chem. Soc., Dalton Trans.*, 2917 (1999).
[15] V.B. Valodkar, G.L. Tembe, M. Ravindranathan, H.S. Rama. *J. Mol. Catal. A: Chem.*, **223**, 31 (2004).
[16] S. Bhor, M.K. Tse, M. Klawonn, C. Doebler, W. Wolfgang, M. Beller. *Adv. Synth. Catal.*, **346**, 263 (2004).
[17] T. Uchida, M. Ohba, T. Katsuki. *Tetrahedron Lett.*, **44**, 7965 (2003).
[18] N. Gunasekaran, N. Remya, S. Radhakrishnan, R. Karvembu. *J. Coord. Chem.*, **64**, 491 (2011).
[19] A.G.F. Shoair. *J. Coord. Chem.*, **65**, 3511 (2012).
[20] R. Rajarao, T.H. Kim, B.R. Bhat. *J. Coord. Chem.*, **65**, 2671 (2012).
[21] S.K. Ghosh, A. Basu, R. Saha, A. Ghosh, K. Mukherjee, B. Saha. *J. Coord. Chem.*, **65**, 1158 (2012).
[22] Z. Nadealian, V. Mirkhani, B. Yadollahi, M. Moghadam, S. Tangestaninejad, I. Mohammadpoor-Baltork. *J. Coord. Chem.*, **65**, 1071 (2012).

[23] M. Bagherzadeh, M. Amini. *J. Coord. Chem.*, **63**, 3849 (2010).
[24] N. Ahmad, J.J. Levison, S.D. Robinson, M.F. Uttley, E.R. Wonchoba, G.W. Parshall. *Inorg. Synth.*, **15**, 45 (1974).
[25] *SMART and SAINT+ for Windows NT (Version 6.02a)*, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA (1998).
[26] G.M. Sheldrick. *SADABS*, University of Göttingen, Germany (1996).
[27] G.M. Sheldrick. *SHELXTL Software Reference Manual. (Version 5.1)*, Bruker AXS Inc., Madison, Wisconsin, USA (1997).
[28] G.M. Sheldrick. *Acta Crystallogr. A*, **64**, 112 (2008).
[29] A.A. Soliman. *Spectrochim. Acta, Part A*, **53**, 509 (1997).
[30] J.L. Pratihar, S. Bhaduri, P. Pattanayak, D. Patra, S. Chattopadhyay. *J. Organomet. Chem.*, **694**, 3401 (2009).
[31] M.M. Tamizh, K. Mereiter, K. Kirchner, R. Karvembu. *J. Organomet. Chem.*, **700**, 194 (2012).
[32] J.G. Małecki. *Polyhedron*, **31**, 159 (2012).
[33] J.G. Małecki, A. Maroń, M. Serda, J. Polański. *Polyhedron*, **56**, 44 (2013).
[34] J.G. Małecki, R. Kruszynski, Z. Mazurak. *Polyhedron*, **28**, 3891 (2009).
[35] X. Liu, Q.F. Zhang, W.H. Leung. *J. Coord. Chem.*, **58**, 1299 (2005).
[36] M.G. Bhowon, H.L.K. Wah, R. Narain. *Polyhedron*, **18**, 341 (1999).
[37] A. Hanyu, E. Takezawa, S. Sakaguchi, Y. Ishii. *Tetrahedron Lett.*, **39**, 5557 (1998).
[38] C.S. Yi, T.N. Zecycki, I.A. Guzei. *Organometallics*, **25**, 1047 (2006).