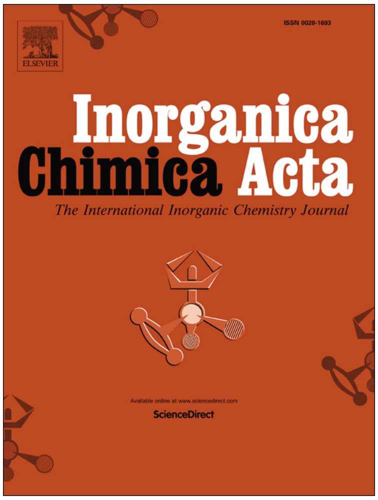

Research paper

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Synthesis, structure and catalytic alcohol oxidation by ruthenium(III) supported by Schiff base and triphenylphosphine ligands

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Treatment of [$RuCl_2(PPh_3)_3$] with two equiv. bi-dentate Schiff base *N,O*-LH-Cl (*N,O*-LH-Cl = 2[(3-chloro-phenylimino)-methyl]-phenol) or *N,O*-LH-NO_2 (*N,O*-LH-NO_2 = 2[(4-nitro-phenylimino)-methyl]-phenol) in the presence of triethylamine afforded *cis*-[$RuCl(PPh_3)(\kappa^2$-*N,O*-L-Cl$)_2$] (**1**) and *trans*-[$RuCl(PPh_3)(\kappa^2$-*N,O*-L-$NO_2)_2$]·Et_2O (**2**), respectively. Reactions of [$RuCl_2(PPh_3)_3$] and equal equiv. tetra-dentate Schiff bases gave corresponding ruthenium(III) complexes [$RuCl(PPh_3)$(salen)] (**3**) (H_2salen = *N*,*N'*-disalicylidene-1,2-ethanediamine), [$RuCl(PPh_3)$(salipn)]·$2CH_2Cl_2$ (**4**) (H_2salipn = *N*,*N'*-disalicylidene-1,2-(1-methyl)ethanediamine), [$RuCl(PPh_3)$(salpn)]·CH_2Cl_2 (**5**) (H_2salpn = *N*,*N'*-disalicylidene-1,2-propanediamine), [$RuCl(PPh_3)$(salphen)]·CH_2Cl_2 (**6**) (H_2salphen = *N*,*N'*-disalicylidene-1,2-phenyldiamine), [$RuCl(PPh_3)$(saltoln)]·CH_2Cl_2 (**7**) (H_2saltoln = *N*,*N'*-disalicylidene-1,2-tolyldiamine) and [$RuCl(PPh_3)$(salcyn)] (**8**) (H_2salcyn = *N*,*N'*-disalicylidene-(*R*,*R*)-1,2-cyclohexanediamine). The molecular structures of complexes **1**–**5** and **7** have been determined by single-crystal X-ray crystallography. The catalytic oxidation properties of ruthenium(III) complexes **1**–**8** were tested towards alcohols in the presence of *N*-methylmorpholine-*N*-oxide.

Keywords: Ruthenium(III) complex; Schiff base; Synthesis; Crystal structure; Catalytic oxidation

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1. Introduction

Ruthenium complexes are extensively being investigated because of their rich structural, electrochemical, catalytic and biological properties [1–3]. In this area, the ruthenium complexes containing *N*,*O*-bidentate and N_2,O_2-tetradentate Schiff bases have been well studied, of which the *N*,*O*-bidentate Schiff base bonded to the ruthenium center in a typically chelating manner forming an approximately coplanar $RuNC_3O$ six-membered ring and the N_2,O_2-tetradentate Schiff base chelated with the ruthenium center forming a stably co-planar RuN_2O_2 square [4–7]. Both bi- and tetra-dentate Schiff bases used in this study have been easily prepared from salicyaldehyde and the substituted mono- or bis-amines [8], in which the phenolic groups are of oxidation property depending on the ruthenium starting materials. The reactions of $Ru^{II}(PPh_3)_3Cl_2$ with the NO/N_2O_2-Schiff bases proceeding *via* oxidative addition are subject to reductive proton elimination, affording motifs of the according ruthenium(III) complexes with the chelating Schiff base ligands [9]. When the staring materials are $K_2Ru^{III}Cl_5(H_2O)$ and $Ru^{III}Cl_3 \cdot xH_2O$, the trivalent ruthenium(III) is unsuitable for oxidative addition and instead gets accordingly NO/N_2O_2-chelated ruthenium(III)/(IV) products at the salicylaldimine sites [10]. Previously, we have reported a series of ruthenium(II) monocarbonyl complexes with *N*,*O*-bidentate Schiff-base ligands and their catalytic behavior towards alcohols [11]. As our long-standing research interest in the high-valence ruthenium complexes, we disclose herein syntheses, structures and catalytic oxidation properties of a series of ruthenium(III) complexes with the coordination type RuN_2O_2PCl supported by Schiff base and triphenylphosphine ligands in this paper.

2. Experimental

2.1. General considerations

All synthetic manipulations were carried out under dry nitrogen by standard Schlenk techniques. Solvents were purified by standard procedures and distilled prior to use. Triethylamine, salicyaldehyde, 3-chloro-phenylamine, 4-nitro-phenylamine, 1,2-ethanediamine, 1-methyl-1,2-ethanediamine, 1,3-propanediamine, 1,2-phenyldiamine, 4-

methyl-1,2-phenyldiamine, and 1,2-cyclohexanediamine were purchased from Alfa Aesar Ltd and used without further purification. The *N*,*O*-bidentate and N_2,O_2-tetradentate Schiff bases (see Chart 1) were prepared by the condensation between salicyaldehyde and according mono- or bis-amines in the refluxing ethanol. $[Ru(PPh_3)_3Cl_2]$ was prepared according to the literature method [12]. Infrared spectra (KBr) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer with use of pressed KBr pellets and positive FAB mass spectra were recorded on a Finnigan TSQ 7000 spectrometer. The magnetic moment for the solid sample was measured by a Sherwood magnetic susceptibility balance at room temperature. Elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer. Gas chromatography (GC) experiments were performed on a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20M. *n*-Decane was used as internal standard and yields were determined by using peak area during the GC testing experiments.

2.2. Synthesis of cis-$[RuCl(PPh_3)(\kappa^2\text{-}N,O\text{-}L\text{-}Cl)_2]$ (**1**)

To a solution of *N*,*O*-LH-Cl (930 mg, 4.0 mmol) in THF (20 mL) was added $[Ru(PPh_3)_3Cl_2]$ (868 mg, 2.0 mmol), which was then stirred under N_2 for 15 min. Triethylamine (Et_3N) (404 mg, 4.0 mmol) was introduced, and the reaction mixture was stirred overnight at room temperature, during which the color of solution changed from brown to dark green. After removal of solvents in *vacuo*, the residue was extracted with CH_2Cl_2 (5 mL ×2) and the solution was filtered. The filtrate was layered with Et_2O (20 mL) at room temperature, and dark green block-shaped crystals of *cis*-$[RuCl(PPh_3)(\kappa^2\text{-}N,O\text{-}L\text{-}Cl)_2]$ (**1**) were harvested in three days. Yield: 1187 mg, 69% (based on Ru). μ_{eff} = 1.98 μ_B. IR (KBr disc, cm^{-1}): 1592 ($\nu_{C=N}$), 1314 (ν_{C-O}), 1437, 1092 and 698 (ν_{PPh_3}). MS (FAB): *m*/*z* 860 $[M^+]$, 825 $[M^+ - Cl]$, 598 $[M^+ - PPh_3]$, 563 $[Ru(\kappa^2\text{-}N,O\text{-}L\text{-}Cl)_2]^+$. *Anal.* Calc. for $C_{44}H_{33}N_2O_2Cl_3PRu$(%): C, 61.44; H, 3.87; N, 3.26. Found: C, 61.47; H, 3.83; N, 3.24.

2.3. Synthesis of trans-$[RuCl(PPh_3)(\kappa^2\text{-}N,O\text{-}L\text{-}NO_2)_2]\cdot Et_2O$ (**2**)

To a solution of $[Ru(PPh_3)_3Cl_2]$ (868 mg, 2.0 mmol) in THF (10 mL) was added a solution of *N*,*O*-LH-NO_2 (972 mg, 2.0 mmol) and Et_3N (404 mg, 4.0 mmol) in EtOH (5 mL), and then the mixture was heated at 90 °C with stirring overnight, during which there was a color change from brown to green. After removal of solvents in *vacuo*, the residue was extracted with CH_2Cl_2 (5 mL ×2) and the solution was filtered. The clearly green filtrate was layered with Et_2O (20 mL) at room temperature, and dark green block-shaped crystals of *trans*-[RuCl(PPh$_3$)(κ^2-*N*,*O*-L-NO$_2$)$_2$]·Et$_2$O (**2**) were obtained in three days. Yield: 1356 mg, 71% (based on Ru). μ_{eff} = 1.97 μ_B. IR (KBr disc, cm^{-1}): 1592 ($\nu_{C=N}$), 1576, 1373 (ν_{NO_2}), 1312 (ν_{C-O}), 1435, 1098 and 694 (ν_{PPh_3}). MS (FAB): *m*/*z* 881 [M$^+$], 846 [M$^+$ − Cl], 619 [M$^+$ − PPh$_3$], 584 [Ru(κ^2-*N*,*O*-L-NO$_2$)$_2$]$^+$. *Anal.* Calc. for $C_{44}H_{33}N_4O_6ClPRu\cdot(C_4H_{10}O)$ (%): C, 60.34; H, 4.54; N, 5.86. Found: C, 60.44; H, 4.51; N, 5.79.

*2.4. Synthesis of [RuCl(PPh$_3$)(salen)] (**3**)*

To a round-bottomed flask with a stir bar was placed with [Ru(PPh$_3$)$_3$Cl$_2$] (868 mg, 2.0 mmol) under the nitrogen. Pre-dried THF (10 mL) was added and the resulting mixture was stirred at room temperature. Then salen-enH$_2$ (536 mg, 2.0 mmol) and a little excess of Et_3N (252 mg, 2.5 mmol) in THF (5 mL) were added. The reaction mixture was stirred at room temperature overnight. After removal of solvents, CH_2Cl_2 (15 mL) was added and the solution was filtered through cilite. The filtrate was concentrated and the residue was washed with Et_2O (5 mL × 2) and hexane (5 mL × 2) to give the desired product. Recrystallization from CH_2Cl_2/Et_2O (1:2) afforded green block-shaped crystals of [RuCl(PPh$_3$)(salen)] (**3**) suitable for X-ray diffraction in three days. Yield: 1011 mg, 76% (based on Ru). μ_{eff} = 1.98 μ_B. IR (KBr disc, cm^{-1}): 1599 ($\nu_{C=N}$), 1317 (ν_{C-O}), 1432, 1085 and 690 (ν_{PPh_3}). MS (FAB): *m*/*z* 665 [M$^+$], 630 [M$^+$ − Cl], 403 [M$^+$ − PPh$_3$], 368 [Ru(salen-en)]$^+$. *Anal.* Calc. for $C_{34}H_{29}N_2O_2ClPRu$ (%): C, 59.97; H, 3.77; N, 6.36. Found: C, 60.05; H, 3.73; N, 6.39.

*2.5. Synthesis of [RuCl(PPh$_3$)(salipn)]·2CH$_2$Cl$_2$ (**4**)*

The method was similar to that used for **3**, employing salen-pnH$_2$ (564 mg, 2.0 mmol) instead of salen-enH$_2$. Yield: 1070 mg, 63% (based on Ru). μ_{eff} = 1.95 μ_B. IR (KBr disc, cm^{-1}): 1594 ($\nu_{C=N}$), 1315 (ν_{C-O}), 1428, 1079 and 692 (ν_{PPh3}). MS (FAB): *m*/*z* 679 [M$^+$], 644 [M^+ – Cl], 417 [M^+ – PPh_3], 382 [Ru(salipn)]$^+$. *Anal.* Calc. for $C_{35}H_{31}N_2O_2ClPRu$·2(CH_2Cl_2) (%): C, 59.42; H, 4.72; N, 3.75. Found: C, 59.63; H, 4.75; N, 3.72.

*2.6. Synthesis of [RuCl(PPh_3)(salpn)]·CH_2Cl_2 (**5**)*

The method was similar to that used for **3**, employing salen-tnH_2 (564 mg, 2.0 mmol) instead of salen-enH_2. Yield: 963 mg, 63% (based on Ru). μ_{eff} = 1.96 μ_B. IR (KBr disc, cm^{-1}): 1598 ($\nu_{C=N}$), 1321 ($\nu_{C–O}$), 1421, 1083 and 699 (ν_{PPh3}). MS (FAB): *m*/*z* 679 [M^+], 644 [M^+ – Cl], 417 [M^+ – PPh_3], 382 [Ru(salpn)]$^+$. *Anal.* Calc. for $C_{35}H_{31}N_2O_2ClPRu$·(CH_2Cl_2) (%): C, 56.59; H, 4.35; N, 3.67. Found: C, 56.53; H, 4.38; N, 3.70.

*2.7. Synthesis of [RuCl(PPh_3)(salphen)]·CH_2Cl_2 (**6**)*

The method was similar to that used for **3**, employing salen-phnH_2 (632 mg, 2.0 mmol) instead of salen-enH_2. Yield: 777 mg, 63% (based on Ru). μ_{eff} = 1.94 μ_B. IR (KBr disc, cm^{-1}): 1591 ($\nu_{C=N}$), 1315 ($\nu_{C–O}$), 1428, 1079 and 692 (ν_{PPh3}). MS (FAB): *m*/*z* 711 [M^+], 676 [M^+ – Cl], 449 [M^+ – PPh_3], 416 [Ru(salphen)]$^+$. *Anal.* Calc. for $C_{38}H_{29}N_2O_2ClPRu$·(CH_2Cl_2) (%): C, 58.69; H, 3.92; N, 3.51. Found: C, 58.74; H, 3.87; N, 3.48.

*2.8. Synthesis of [RuCl(PPh_3)(saltoln)]·CH_2Cl_2 (**7**)*

The method was similar to that used for **3**, employing salen-tolnH_2 (660 mg, 2.0 mmol) instead of salen-enH_2. Yield: 1039 mg, 64% (based on Ru). μ_{eff} = 1.96 μ_B. IR (KBr disc, cm^{-1}): 1591 ($\nu_{C=N}$), 1318 ($\nu_{C–O}$), 1423, 1071 and 697 (ν_{PPh3}). MS (FAB): *m*/*z* 727 [M^+], 692 [M^+ – Cl], 465 [M^+ – PPh_3], 430 [Ru(saltoln)]$^+$. *Anal.* Calc. for $C_{39}H_{31}N_2O_2ClPRu$·(CH_2Cl_2) (%): C, 59.16; H, 4.10; N, 3.45. Found: C, 59.13; H, 4.04; N, 3.51.

*2.9. Synthesis of [RuCl(PPh_3)(salcyn)] (**8**)*

The method was similar to that used for **3**, employing salen-*R*,*R*'-cynH_2 (644 mg, 2.0 mmol) instead of salen-enH_2. Yield: 818 mg, 57% (based on Ru). μ_{eff} = 1.99 μ_B. IR (KBr disc, cm^{-1}): 1590 ($\nu_{C=N}$), 1308 ($\nu_{C–O}$), 1411, 1074 and 696 (ν_{PPh3}). MS (FAB): *m*/*z* 718

[M^+], 683 [M^+ – Cl], 456 [M^+ – PPh_3], 421 [Ru(salcyn)]$^+$. *Anal.* Calc. for $C_{38}H_{34}N_2O_2ClPRu$ (%): C, 63.55; H, 4.77; N, 3.90. Found: C, 63.53; H, 4.76; N, 3.94.

2.10. X-ray crystallography

A summary of crystallographic data and experimental details for complexes **1–5** and **7** are 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 the software SAINT [13]. The data was corrected for absorption using the program SADABS [14]. Structures were solved by the direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [15,16]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms 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 displacement parameters but were not refined.

2.11. Procedure for catalytic oxidation of alcohols

Oxidations of primary alcohols to aldehydes and secondary ones to ketones were catalyzed by complexes **1–8** in the presence of *N*-methylmorpholine-*N*-oxide (NMO) as co-oxidant. A typical reaction using complexes **1–8** as catalysts is as follows. A solution of each of complexes **1–8** (0.01 mmol) in 10 mL of CH_2Cl_2 was added to the mixture of substrate (1 mmol) and NMO (2 mmol). The mixture was stirred at room temperature for 12 h and the solvent was evaporated under reduced pressure with a rotary evaporator resulting in a solid mass. Then 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

As shown in Scheme 1, interaction of [$RuCl_2(PPh_3)_3$] with two equiv. Schiff base ligand *N,O*-LH-Cl at room temperature in the presence of organic base afforded *cis*-[$RuCl(PPh_3)(\kappa^2$-*N,O*-L-Cl$)_2$] (**1**), while the similar reaction employing *N,O*-LH-NO_2 compound occurred at 90 °C resulted in formation of *trans*-[$RuCl(PPh_3)(\kappa^2$-*N,O*-L-

$NO_2)_2]\cdot Et_2O$ (**2**). It appears that reaction of [$RuCl_2(PPh_3)_3$] with *N*,*O*-bidentate Schiff bases may probably depend on thermo-dynamic conditions such as reactive temperature and solvent, which will be needed more examples to explain the relationship between reaction conditions and substituted groups of *N*,*O*-bidentate Schiff base ligands [17]. Reactions of [$RuCl_2(PPh_3)_3$] and equal equiv. tetra-dentate Schiff bases gave corresponding ruthenium(III) complexes with *O*$_2$,*N*$_2$-salen ligands, [$RuCl(PPh_3)$(salen)] (**3**), [$RuCl(PPh_3)$(salipn)]$\cdot 2CH_2Cl_2$ (**4**), [$RuCl(PPh_3)$(salpn)]$\cdot CH_2Cl_2$ (**5**), [$RuCl(PPh_3)$(salphen)]$\cdot CH_2Cl_2$ (**6**), [$RuCl(PPh_3)$(saltoln)]$\cdot CH_2Cl_2$ (**7**) and [$RuCl(PPh_3)$(salcyn)] (**8**). Two PPh_3 ligands and one chloride in the starting ruthenium(II) compound were just replaced by two bidentate *O*,*N*-ligands or one tetradentate *O*$_2$,*N*$_2$-ligand in the present reaction system, thus, the anionic bidentate *O*,*N*-ligands or tetradentate *O*$_2$,*N*$_2$-ligands bind the ruthenium(III) centre. IR spectra of all Schiff base ligands showed a strong band in the region 1590−1599 cm^{-1} which is characteristic of the -CH=N- group absorptions. Absorption due to phenolic O−H was not observed in the IR spectra of all the complexes, suggesting deprotonation prior to coordination to the ruthenium atom. The C–O stretching vibration modes were found at around 1315 cm^{-1} in the IR spectra of complexes **1**–**8**. The effective magnetic moment μ_{eff} of 1.94–1.99 μ_B at room temperature is consistent with a ruthenium(III) formulation for complexes **1**–**8** [18]. The positive ion FAB mass spectra of **1−8** display the expected peaks corresponding to the molecular ions {[M^+], [M^+ − Cl] or [M^+ − PPh_3], and [ML_2]$^+$, or [ML]$^+$ } with the characteristic isotopic distribution patterns.

The structures of complexes **1**–**5** and **7** have been established by X-ray crystallography. The perspective views of the molecular structures of **1**–**5** and **7** are shown in Figs. 1−6, respectively, with atom numbering scheme. Selected bond lengths and bond angles for complexes **1**–**5** and **7** are summarized in Table 2 for the comparison. The central ruthenium atom in complexes **1**–**5** and **7** is in an octahedral coordination environment, containing two bidentate ligands or one tetradentate ligand with the bite N−Ru−O angles (av. 90.7(1)°). The triphenylphosine ligand and chloro ligand are *cis* in **1** with the P−Ru−Cl angle of 93.51(2)°, which is compared with that in few reported

RuN_2O_2PCl complexes [Ru(κ^2-*N,O*-L)$_2$(PPh_3)Cl] (L = 3-ethyliminomethyl-2-hydroxy-5-methyl-benzaldehyde, 90.2(1)°) [10], [RuCl(bsp)$_2$(PPh_3)] (Hbsp = [*N*-(2-hydroxybenzylidene)-benzothiazole, 92.37°) [17], [Ru(PPh_3)Cl(PhenoxSQ)$_2$] (HPhenoxSQ = 1-hydroxy-2,4,6,8-tetra-*tert*-butylphenoxazinyl radical, 99.8(1)°) [19]. The P–Ru–Cl angles (average value of 176.52(3)°) in complexes **2**–**5** and **7** are well in the range of other RuN_2O_2PCl complexes [RuCl(PPh_3){sal-(*RR*)-chxn}] (H_2sal-(*RR*)-chxn = *N*,*N'*-disali-cylidene-(*R*,*R*)-1,2-cyclohexanediamine, 173.7(3)°) [6] and [(OL)Ru(PPh_3)Cl] (OL = azosalen, 179.07(2)°) [20]. The Ru–P and Ru–Cl bond lengths in *cis*-[RuCl(PPh_3)(κ^2-*N,O*-L-Cl)$_2$] **1** (2.3489(5) and 2.3691(5) Å) are a little shorter than those in complex **2** (2.4063(8) and 2.4290(8) Å). The average Ru–N and Ru–O bond lengths in complexes **1** and **2** are 2.094(2) and 1.988(2) Å, respectively, which are similar to those in salen-type ruthenium(III) complexes **3**–**5** and **7** (av. Ru–N = 2.004(4) Å and av. Ru–O = 2.009(3) Å), indicating the bi- and tetra-dentate Schiff base ligands have little difference in coordinating ability to the ruthenium(III) center.

Ruthenium(III) complexes **1**–**8** have been found to catalyze oxidation of primary alcohols to corresponding aldehydes and secondary alcohols to ketones in dichloromethane in the presence of NMO (Scheme 2). Various alcohols have been selectively converted into corresponding aldehydes or ketones with 1 mol% of the ruthenium(III)-Schiff complex catalysts. It has been observed that neither the present complex nor NMO alone causes this organic transformation under identical reaction conditions. The precursor complex [Ru(PPh_3)$_3$$Cl_2$] showed less catalytic property compared with the present ruthenium(III)-Schiff complexes bearing bi- or tetra-dentate Schiff base and triphenylphosphine ligands. The TON (%conversion) values are given in Table 3, which showed that all the substrates were efficiently converted to the corresponding ketones or aldehydes. Substituted benzylic primary alcohols bearing electron-donating and electron-withdrawing groups all afforded the corresponding aldehydes in good conversions that seem no obvious difference. Benzylic secondary alcohols were found to be smoothly oxidized to the corresponding ketones with moderate yields. No further oxidation of aldehydes to acids was observed even after extended reaction time. The efficiency of oxidation of benzylic alcohols is higher than already reported catalytic systems of [RuX(EPh$_3$)L] (where X = Cl/Br; E = P/As; and L = dibasic tetradentate Schiff base derived by condensation of ethylenediamine with acetoacetanilide/acetoacetotoluidide-/ethylacetoacetate) [21] and is well compared with binuclear ruthenium(III) bis(thiosemicarbazone) complexes [22]. Unlike benzylic alcohols, the conversion was not encouraging in the case of cyclohexanol and 1-cyclohexylethanol which were converted into their corresponding ketones in 72%–80% yields. The investigations to understand further catalytic mechanics and properties of the ruthenium(III) complexes containing bidentate and tetradentate Schiff base ligands are in progress.

In summary, a series of ruthenium(III) complexes with bi- or tetradentate Schiff base ligands were synthesized and characterized from ruthenium(II) starting compound [RuCl$_2$(PPh$_3$)$_3$], confirming the much or less oxidative property of Schiff bases towards [RuCl$_2$(PPh$_3$)$_3$] [9]. The different chloro and nitro substituted groups at bidentate Schiff base ligands lead to different geometries of the according ruthenium(III) complexes *cis*-[RuCl(PPh$_3$)(κ^2-*N,O*-L-Cl)$_2$] **1** and *trans*-[RuCl(PPh$_3$)(κ^2-*N,O*-L-NO$_2$)$_2$]·Et$_2$O **2**. The ruthenium(III) complexes **1**–**8** exhibited obviously catalytic performance on oxidation of alcohols to corresponding aldehydes or ketones in the presence of NMO co-oxidant, 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 relatively mild conditions.

Supplementary material

Crystallographic data for **1**–**5** and **7** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1573974-1573979, 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; e-mail: deposit@ccdc.cam.ac.uk].

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References

[1] J. Kothandaraman, A. Goeppert, M. Czaun, G.A. Olah, G. K. S. Prakash, J. Am. Chem. Soc. 138 (2016) 778.

[2] J.R. Johansson, T. Beke-Somfai, A.S. Stalsmeden, N. Kann, Chem. Rev. 116 (2016) 14726.

[3] J. Furrer, G. Suss-Fink, Coord. Chem. Rev. 309 (2016) 36.

[4] W.-G. Jia, H. Zhang, T. Zhang, D. Xie, S. Ling, E.H. Sheng, Organometallics 35 (2016) 503.

[5] R. Prabhakaran, R. Huang, K. Natarajan, Inorg. Chim. Acta 359 (2006) 3359.

[6] K. Nakajima, Y. Ando, H. Mano, M. Kojima, Inorg. Chim. Acta 274 (1998) 184.

[7] Y. Li, Q. Ma, H.-T. Shi, Q. Chen, Q.-F. Zhang, Z. Naturforsch. 66b (2011) 324.

[8] J.F. Larrow, E.N. Jacobsen, J. Org. Chem. 59 (1994) 1939.

[9] S. Bhattacharya, S.R. Boone, C.G. Pierpont, J. Am. Chem. Soc. 112 (1990) 4561.

[10] S. Pattanayak, K. Pramanik, N. Bag, P. Ghosh, A. Chakravorty, Polyhedron 16 (1997) 2951.

[11] X.-F. Yin, H. Lin, A.-Q. Jia, Q. Chen, Q.-F. Zhang, J. Coord. Chem. 66 (2013) 3229.

[12] T.A. Stephenson, G. Wilkinson, J. Inorg. Nucl. Chem. 28 (1996) 945.

[13] *SMART and SAINT+ for Windows NT Version 6.02a*. Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA (1998).

[14] G. M. Sheldrick, *SADABS*. University of Göttingen, Germany (1996).

[15] G. M. Sheldrick, *SHELXTL Software Reference Manual. Version 5.1*. Bruker AXS Inc., Madison, Wisconsin, USA (1997).

[16] G. M. Sheldrick, Acta Crystallogr. A 64 (2008) 112.

[17] I.N. Booysen, A. Adebisi, O.Q. Munro, B. Xulu, Polyhedron 73 (2014) 1.

[18] P.M. Chan, W.Y. Yu, C.M. Che, K.K. Cheung, J. Chem. Soc., Dalton Trans. (1998) 3183.

[19] S. Bhattacharya, C.G. Pierpont, Inorg. Chem. 31 (1992) 2020.

[20] P. Pattanayak, D. Patra, J.L. Pratihar, A. Burrows, M.F. Mahon, S. Chattopadhyay, Inorg. Chim. Acta 363 (2010) 2865.

[21] N.P. Priya, S. Arunachalam, N. Sathya, C. Jayabalakrishnan. J. Coord. Chem. 63 (2010) 1440.

[22] M.M. Subarkhan, R. Ramesh. Spectrochim Acta A 138 (2015) 264.

Table 1. Crystallographic data and experimental details for *cis*-[RuCl(PPh$_3$)(κ^2-*N*,*O*-L-Cl)$_2$] (**1**), *trans*-[RuCl(PPh$_3$)(κ^2-*N*,*O*-L-NO$_2$)$_2$]·Et$_2$O (**2**), [RuCl(PPh$_3$)(salen)] (**3**), [RuCl(PPh$_3$)(salipn)]·2CH$_2$Cl$_2$ (**4**), [RuCl(PPh$_3$)(salpn)]·CH$_2$Cl$_2$ (**5**), and [RuCl(PPh$_3$)(saltoln)]·CH$_2$Cl$_2$ (**7**).

Complex	**1**	**2**	**3**	**4**	**5**	**7**
Empirical formula	$C_{44}H_{33}N_2O_2Cl_3PRu$	$C_{48}H_{43}N_4O_7ClPRu$	$C_{34}H_{29}N_2O_2ClPRu$	$C_{37}H_{35}N_2O_2Cl_5PRu$	$C_{36}H_{33}N_2O_2Cl_3PRu$	$C_{40}H_{33}N_2O_2Cl_3PRu$
Formula weight	860.11	955.35	665.08	848.96	764.03	812.07
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
a (Å)	8.6244(7)	13.823(2)	11.0725(4)	14.629(3)	9.2508(3)	14.2537(18)
b (Å)	11.6785(10)	16.702(3)	21.2498(7)	13.910(2)	34.8344(10)	13.7095(17)
c (Å)	20.768(2)	20.431(3)	12.7703(4)	18.647(3)	11.4042(3)	18.923(2)
α (°)	101.232(1)					
β (°)	96.151(1)	107.047(2)	101.966(2)	103.163(4)	112.641(2)	103.596(2)
γ (°)	110.548(1)					
V (Å^3)	1885.8(3)	4509.6(12)	2939.41(17)	3694.8(11)	3391.75(17)	3594.1(8)
Space group	P-1	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$
Z	2	4	4	4	4	4
D_{calc} (g cm^{-3})	1.515	1.407	1.503	1.526	1.496	1.501
Temperature (K)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)
F(000)	874	1964	1356	1724	1556	1652
μ(Mo-Kα) (mm^{-1})	0.712	0.498	0.713	0.865	0.781	0.742
Total refln	11850	26800	29366	23173	32908	22060
Independent refln	8354	10086	6790	8322	7691	8160

Parameters	478	561	370	434	406	443
R_{int}	0.0131	0.0237	0.0599	0.0649	0.0434	0.0600
$R1^{a}$, $wR2^{b}$ ($I > 2\sigma(I)$)	0.0287, 0.0663	0.0358, 0.0836	0.0428, 0.0789	0.0779, 0.1097	0.0560, 0.1040	0.0562, 0.1377
$R1$, $wR2$ (all data)	0.0338, 0.0691	0.0606, 0.1020	0.0852, 0.0921	0.1009, 0.1486	0.0673, 0.1253	0.1095, 0.1647
GoF[c]	1.016	1.077	1.016	1.025	0.970	1.035

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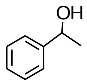
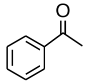
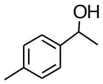
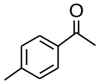
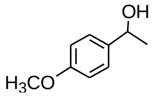
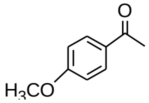
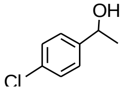
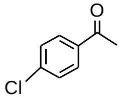
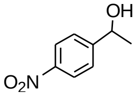
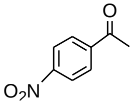
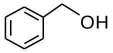
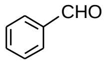
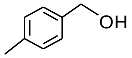
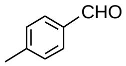
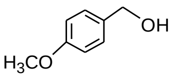
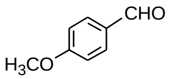
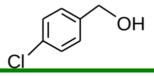
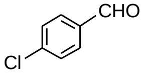
[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.
[c] GoF = $[\Sigma w(|F_o| - |F_c|)^2/(N_{\mathrm{obs}} - N_{\mathrm{param}})]^{1/2}$.

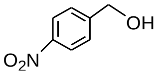
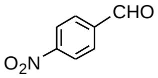
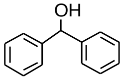
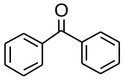
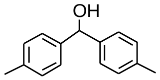
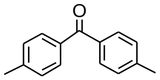
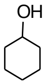
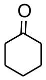
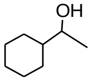
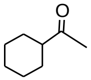
Table 2.

Selected bond lengths (Å) and angles (°) for complexes **1**–**5** and **7**.

complex	Ru–N	Ru–O	Ru–P	Ru–Cl	N–Ru–O	Cl–Ru–P
1	2.0890(16)	2.0215(13)	2.3489(5)	2.3691(5)	89.10(6)	93.51(2)
	2.1469(16)	1.9735(13)			88.95(6)	
2	2.076(2)	1.9814(17)	2.4063(8)	2.4290(8)	91.07(8)	177.41(3)
	2.062(2)	1.9759(17)			90.24(8)	
3	1.986(3)	2.011(2)	2.3507(9)	2.4423(9)	90.60(10)	177.86(3)
	1.992(3)	2.022(2)			90.36(10)	
4	2.009(5)	2.015(4)	2.3377(16)	2.4468(18)	90.74(19)	176.06(7)
	1.987(6)	2.015(4)			90.8(2)	
5	2.035(4)	2.007(3)	2.3659(11)	2.4223(12)	89.58(15)	175.88(4)
	2.052(4)	2.014(3)			91.10(14)	
7	2.017(4)	2.004(3)	2.3442(13)	2.4455(13)	92.60(14)	176.09(5)
	2.005(4)	2.013(3)			91.08(14)	

Table 3. Oxidation of alcohols of corresponding aldehydes and ketones with NMO co-oxidant catalyzed by complexes **1–8**[a]

Entry	Substrate	Product	TON[b] (% conversions[c])[d]							
			1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
1			785(74)	765(72)	801(77)	809(78)	795(75)	823(82)	849(81)	836(80)
2			772(73)	753(70)	791(76)	804(80)	812(78)	816(77)	902(86)	892(85)
3			782(78)	779(75)	805(79)	835(83)	830(79)	843(84)	887(82)	875(82)
4			782(78)	779(75)	805(79)	835(83)	830(79)	843(84)	887(82)	875(82)
5			802(81)	841(84)	837(83)	896(87)	821(82)	809(80)	892(86)	883(85)
6			1004(90)	1012(92)	992(91)	1102(94)	998(89)	926(88)	1006(89)	1108(93)
7			1220(93)	1158(95)	1109(94)	1004(91)	972(90)	996(93)	1162(92)	1247(95)
8			1215(91)	1126(92)	1002(91)	985(89)	994(92)	1019(95)	1271(95)	1118(91)
9			980(88)	1073(90)	972(86)	959(87)	992(91)	1006(93)	1126(92)	1083(90)

10			1124(92)	1233(93)	1039(90)	974(88)	987(93)	1234(95)	1089(93)	1025(91)
11			891(85)	810(82)	883(87)	928(90)	949(91)	910(89)	916(85)	887(88)
12			899(86)	852(84)	819(83)	902(91)	915(88)	903(86)	913(87)	854(84)
13			692(79)	637(77)	784(79)	814(80)	825(80)	810(80)	721(79)	713(78)
14			627(73)	610(74)	604(72)	783(77)	793(80)	629(75)	637(76)	794(79)

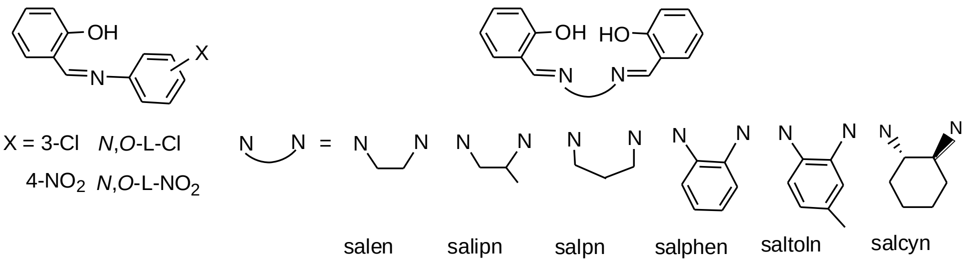
[a] Reaction conditions: alcohol (1 mmol), NMO (2 mmol), catalyst (0.01 mmol), dichloromethane (20 mL), stirring for 12 h, room temperature.

[b] TON is a ratio of mmol of product/mmol of catalyst.

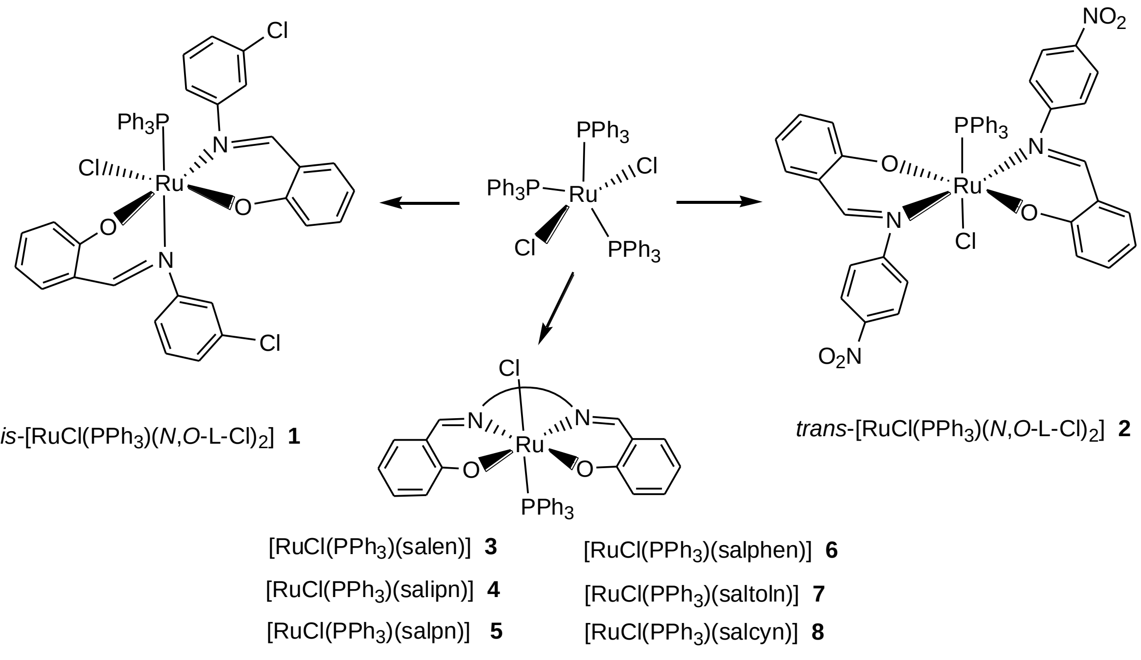
[c] Conversions (%) are measured relative to the starting alcohol after 12 h.

[d] Yield is determined by GC with area normalization.

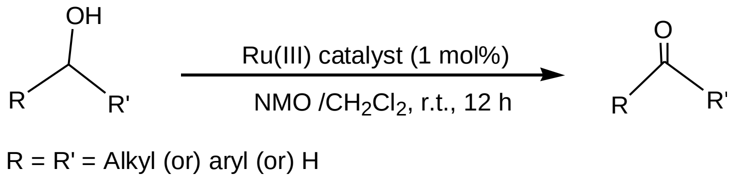
Chart 1. Schematic of *N,O*-LH-Cl, *N,O*-LH-NO_2, and series salen-type ligands.



Scheme 1. Synthesis of ruthenium(III) complexes **1**–**8**.



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



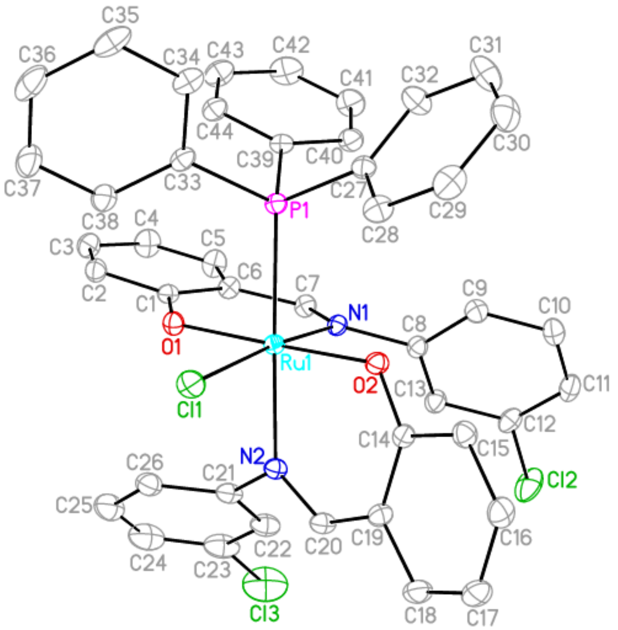


Fig. 1. Molecular structure of *cis*-[RuCl(PPh$_3$)(κ^2-*N*,*O*-L-Cl)$_2$] (**1**), showing the atom labeling scheme and 40% displacement parameters. Hydrogen atoms are omitted for clarity.

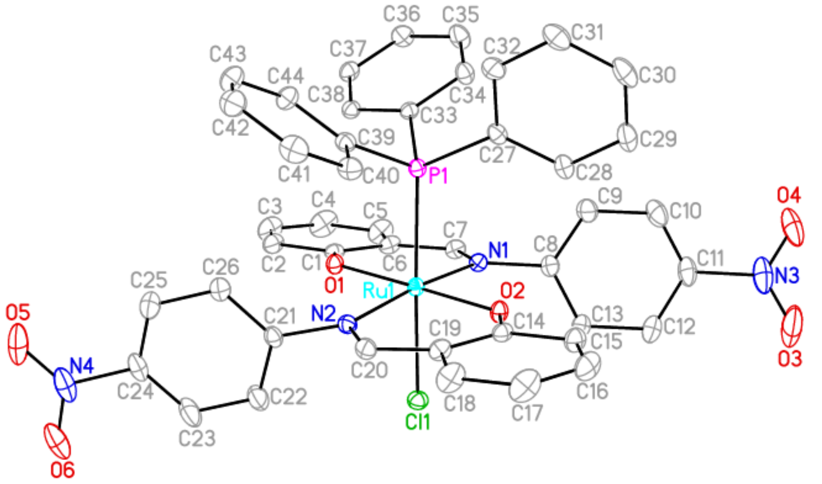


Fig. 2. Molecular structure of *trans*-[RuCl(PPh$_3$)(κ^2-*N*,*O*-L-NO$_2$)$_2$]·Et$_2$O (**2**), showing the atom labeling scheme and 40% displacement parameters. Hydrogen atoms and solvent are omitted for clarity.

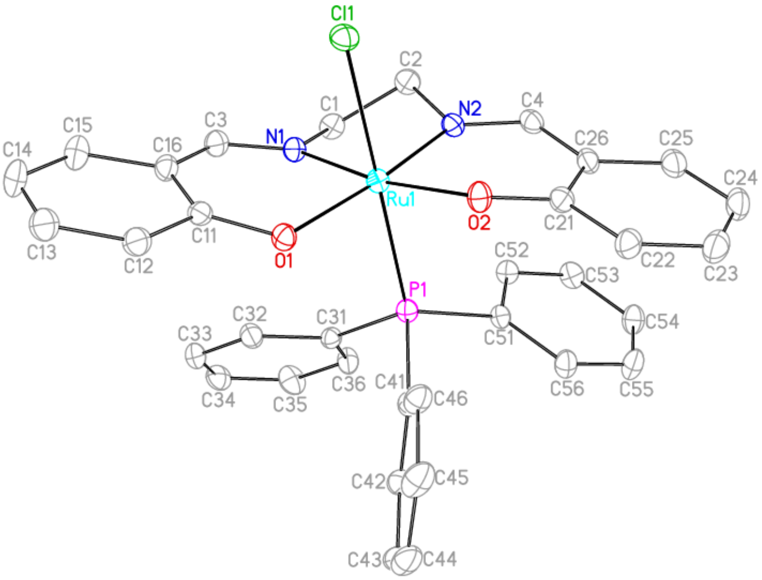


Fig. 3. Molecular structure of [RuCl(PPh$_3$)(salen)] (**3**), showing the atom labeling scheme and 40% displacement parameters. Hydrogen atoms are omitted for clarity.

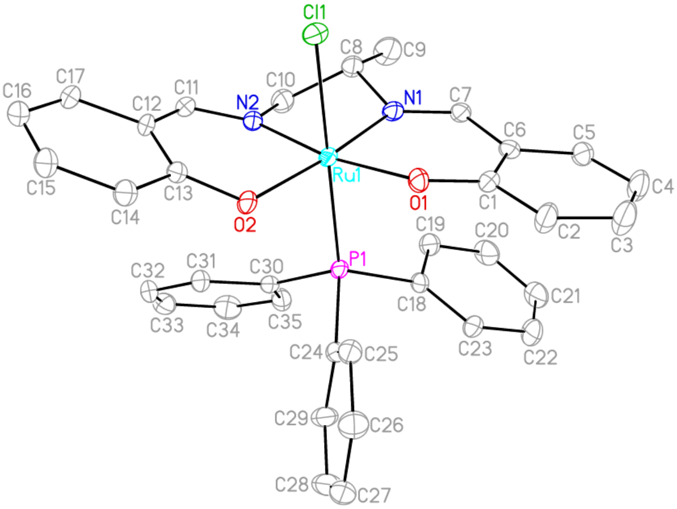


Fig. 4. Molecular structure of [RuCl(PPh$_3$)(salipn)]·2CH$_2$Cl$_2$ (**4**), showing the atom labeling scheme and 40% displacement parameters. Hydrogen atoms and solvent are omitted for clarity.

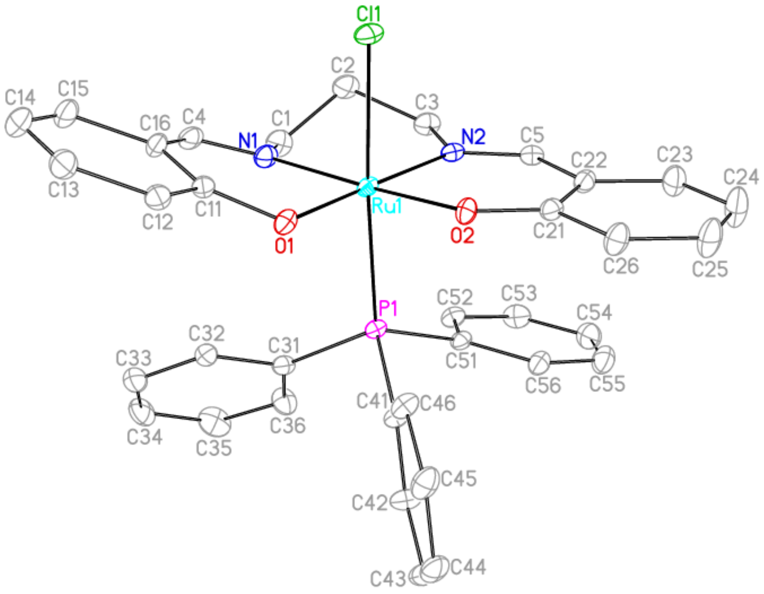


Fig. 5. Molecular structure of [RuCl(PPh$_3$)(salpn)]·CH$_2$Cl$_2$ (**5**), showing the atom labeling scheme and 40% displacement parameters. Hydrogen atoms and solvent are omitted for clarity.

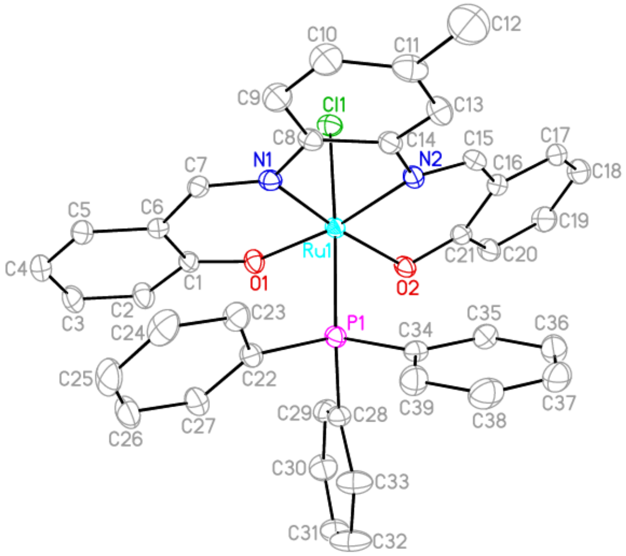


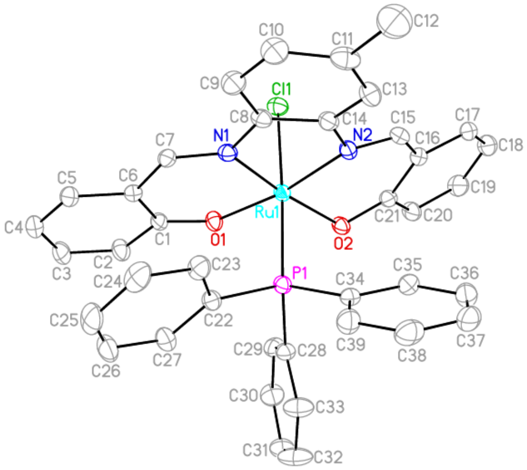
Fig. 6. Molecular structure of [RuCl(PPh$_3$)(saltoln)]·CH$_2$Cl$_2$ (**7**), showing the atom labeling scheme and 40% displacement parameters. Hydrogen atoms and solvent are omitted for clarity.

Graphical Abstract

Synthesis, structure and catalytic alcohol oxidation by ruthenium(III) supported by Schiff base and triphenylphosphine ligands

Li-Hua Tang, Fule Wu, Hui Lin, Ai-Quan Jia, and Qian-Feng Zhang*

Ruthenium(III) complexes with *N*,*O*-bidentate and N_2,O_2-tetradentate Schiff base ligands are synthesized from [Ru(PPh_3)$_3$$Cl_2$] in the refluxing tetrahydrofuran. The catalytic oxidation properties of these ruthenium(III) complexes were tested towards the substituted alcohols.



Highlights

► Reactions of [$RuCl_2(PPh_3)_3$] and Schiff bases afford a series of Ru(III) complexes. ► Ruthenium complexes with bi- and tetra-dentate Schiff bases were fully characterized. ► The ruthenium(III) complexes were tested as catalyst for oxidation of alcohols.