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Synthesis, structural characterization and catalytic activity of chlororuthenium(II) complexes with substituted Schiff base/phosphine ancillary ligands

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Abstract: Treatment of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with one equivalent of chlorodiphenylphosphine in tetrahydrofuran at reflux afforded a neutral complex $[(\eta^6\text{-}p\text{-cymene})RuCl_2(\kappa^1\text{-}P\text{-}PPh_2OH)]$ (**1**). Similarly, the reaction of $[Ru(bpy)_2Cl_2{\cdot}2H_2O]$ (bpy = 2,2′-bipyridine) and chlorodiphenylphosphine in methanol gave a cationic complex $[Ru(bpy)_2Cl(\kappa^1\text{-}P\text{-}PPh_2OCH_3)](PF_6)$ (**2**), while treatment of $[RuCl_2(PPh_3)_3]$ with $[2\text{-}(C_5H_4N)CH{=}N(CH_2)_2N(CH_3)_2]$ (**L1**) in tetrahydrofuran at room temperature afforded a ruthenium(II) complex $[Ru(PPh_3)Cl_2(\kappa^3\text{-}N,N,N\text{-}\mathbf{L1})]$ (**3**). Interaction of the chloro-bridged complex $[Ru(CO)_2Cl_2]_n$ with one equivalent of $[Ph_2P(o\text{-}C_6H_4)CH{=}N(CH_2)_2N(CH_3)_2]$ (**L2**) led to the isolation of $[Ru(CO)Cl_2(\kappa^3\text{-}P,N,N\text{-}\mathbf{L2})]$ (**4**). The molecular structures of the ruthenium(II) complexes **1**–**4** have been determined by single-crystal X-ray crystallography. The properties of the ruthenium(II) complex **4** as a hydrogenation catalyst for acetophenone were also tested.

Keywords: catalytic hydrogenation; crystal structure; phosphine ligand; ruthenium; Schiff base; synthesis.

1 Introduction

Organic phosphines are a very important and widely used class of ligands in coordination chemistry, materials chemistry and organic synthesis [1–3]. Transition metal complexes with phosphine ligands are among the most common and efficient catalysts due to the possibility of fine-tuning the electronic and steric properties of the coordinating ligands [4, 5]. In particular, a series of metal catalysts of ruthenium(II) complexes containing monodentate ($\kappa^1\text{-}P$), bidentate ($\kappa^2\text{-}P,P$, $\kappa^2\text{-}P,N$) or tetradentate ($\kappa^4\text{-}P_2N_2$, $\kappa^4\text{-}P_2O_2$) phosphine ligands have been reported [6–8]. Meanwhile, it has been demonstrated that ruthenium(II) complexes bearing Schiff base ligands are also excellent catalysts in organic synthesis [9]. Contrary to the frequently studied phosphine ligands, Schiff base ligands are not only available by a relatively simple single-step synthetic procedure, but also offer a valuable structural ligand diversity. We extend our interest to Schiff base ligands which contain two nitrogen atoms, with the expectation of exploiting their new reactivity. Moreover, it may be interesting to develop nitrogen-containing ruthenium(II) complexes in which phosphorus atoms are offered in ancillary ligands for chelation. Previously, we have reported a series of ruthenium complexes bearing phosphine ligands with methoxysilyl groups [10]. We herein describe syntheses and structures of four novel ruthenium(II) complexes $[(\eta^6\text{-}p\text{-cymene})RuCl_2(\kappa^1\text{-}P\text{-}PPh_2OH)]$ (**1**), $[Ru(bpy)_2Cl(\kappa^1\text{-}P\text{-}PPh_2OCH_3)](PF_6)$ (**2**), $[Ru(PPh_3)Cl_2(\kappa^3\text{-}N,N,N\text{-}\mathbf{L1})]$ (**3**) and $[Ru(CO)Cl_2(\kappa^3\text{-}P,N,N\text{-}\mathbf{L2})]$ (**4**). The catalytic activity of complex **4** in hydrogenation reactions was also investigated.

2 Experimental section

2.1 General

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, *N*,*N*-dimethylethylenediamine, 2-pyridinecarboxaldehyde, 2-(diphenylphosphino)benzaldehyde and chlorodiphenylphosphine were purchased from Alfa Aesar Ltd and used without further purification. The starting ruthenium complexes $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ [11], $[Ru(bpy)_2Cl_2{\cdot}2H_2O]$ (bpy = 2,2′-bipyridine) [12], $[RuCl_2(PPh_3)_3]$ [13] and $[Ru(CO)_2Cl_2]_n$ [14] were prepared according to literature methods. NMR spectra were

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recorded on a Bruker ALX 400 Plus spectrometer operating at 400 and 162 MHz for ^{1}H and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^{1}H) and H_3PO_4 (^{31}P). Infrared spectra (KBr) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer with use of pressed KBr pellets. Gas chromatographic analyses were performed with an FID detector on a Shimadzu GC-2010 Plus spectrometer using the RTX-5 column (15 m × 0.25 mm, film thickness 0.25 μm). The initial temperature of the column was 110 °C and increased to 260 °C with a rate of 20 K min^{-1}. Elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer.

2.2 Synthesis of [2-(C_5H_4N)CH=N(CH_2)$_2$N(CH_3)$_2$] (L1)

An oven-dried glass flask charged with 2-pyridinecarboxaldehyde (107 mg, 1.0 mmol) and *N*,*N*-dimethylethylenediamine (88 mg, 1.0 mmol) in toluene (30 mL), was heated at reflux with stirring overnight, during which time there was a color change from yellow-brown to dark red. After removal of solvent in *vacuo*, the residue was washed with diethyl ether (3 × 5 mL). Recrystallization from dichloromethane-diethyl ether afforded a dark red solid (**L1**). Yield: 158 mg, 89%. – ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.56 (dd, J = 4.8, 0.7 Hz, 1H, pyridine), 8.34 (s, 1H, CH=N), 7.91 (d, J = 7.9 Hz, 1H, pyridine), 7.64 (m, 1H, pyridine), 7.21 (dd, J = 7.5, 1.2 Hz, 1H, pyridine), 3.74 (td, 7.1, 1.4 Hz, 2H, CH_2), 2.62 (t, J = 6.9 Hz, 2H, CH_2), 2.37 (s, 6H, N(CH_3)$_2$). – IR (KBr disc, cm^{-1}): ν(C=N) 1648 (s), ν(C–N) 1089 (vs), 1082 (s). – Anal. calc. for $C_{10}H_{15}N_3$: C 67.76, H 8.53, N 23.71; found C 67.77, H 8.51, N 23.72%.

2.3 Synthesis of [Ph_2P(*o*-C_6H_4)CH=N(CH_2)$_2$N(CH_3)$_2$] (L2)

A toluene (25 mL) solution of *N*,*N*-dimethylethylenediamine (88 mg, 1.0 mmol) was added to 2-(diphenylphosphino)benzaldehyde (290 mg, 1.0 mmol) in a round-bottomed flask equipped with a condenser. The reaction mixture was stirred at reflux for 12 h. After the completion of reaction, the solvent was pumped off and the residue was washed with diethyl ether (3 × 5 mL). Recrystallization from dichloromethane-diethyl ether gave a red solid (**L2**). Yield: 318 mg, 88%. – ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.82 (d, J = 4.8 Hz, 1H, CH=N), 7.88 (d, J = 7.2 Hz, 1H, Ar-*H*), 7.68 (d, J = 3.6 Hz, 1H, Ar-*H*), 7.60–7.53 (m, 1H, Ar-*H*), 7.50–7.44 (m, 1H, Ar-*H*), 7.42–7.36 (m, 1H, Ar-*H*), 7.25–7.16 (m, 8H, Ar-*H*), 6.78 (d, J = 7.7 Hz, 1H, Ar-*H*), 3.57 (d, J = 6.9 Hz, 2H, CH_2), 2.39 (d, J = 3.3 Hz, 2H, CH_2), 2.17 (d, J = 2.0 Hz, 6H, N(CH_3)$_2$). – ^{31}P NMR (162 MHz, $CDCl_3$, ppm): δ = –13.62 (s, PPh_2). – IR (KBr disc, cm^{-1}): ν(C=N) 1640 (s), ν(C–N) 1092 (vs), 1024 (vs). – Anal. calc. for $C_{23}H_{25}N_2P$: C 76.64, H 6.99, N 7.77; found C 76.65, H 6.98, N 7.76%.

2.4 Synthesis of [(η^6-*p*-cymene)$RuCl_2$(κ^1-*P*-PPh_2OH)] (1)

To a solution of [(η^6-*p*-cymene)$RuCl_2$]$_2$ (62 mg, 0.10 mmol) in tetrahydrofuran (30 mL) was added a solution of chlorodiphenylphosphine (44 mg, 0.20 mmol) in tetrahydrofuran (5 mL), and then the mixture was heated at 90 °C for 4 h, during which time there was a color change from orange to dark red. After removal of solvent in *vacuo*, the residue was washed with diethyl ether (2 × 5 mL) and *n*-hexane (2 × 5 mL) and dissolved in dichloromethane (4 mL). The filtrate was layered with *n*-hexane (20 mL) at room temperature, and dark red block-shaped crystals of product (**1**) were obtained in five days. Yield: 38 mg, 75% (based on ruthenium). – ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.75–7.64 (m, 5H, Ar-*H*), 7.56–7.40 (m, 5H, Ar-*H*), 6.62 (s, 1H, PO–H), 5.40 (d, J = 6.9 Hz, 2H, *p*-cymene), 5.26 (d, J = 6.0 Hz, 2H, *p*-cymene), 2.51 (s, 1H, CH), 2.01 (s, 3H, CH_3), 0.98 (d, J = 7.0 Hz, 6H, CH(CH_3)$_2$). – ^{31}P NMR (162 MHz, $CDCl_3$, ppm): δ = 105.7 (s, (OH)PPh_2). – IR (KBr disc, cm^{-1}): ν(O–H) 3223 (m), ν(P–O) 860 (w). – Anal. calc. for $C_{22}H_{25}OCl_2PRu$: C 51.98, H 4.96; found C 51.95, H 4.96%.

2.5 Synthesis of [$Ru(bpy)_2Cl$(κ^1-*P*-PPh_2OCH_3)](PF_6) (2)

To a solution of [$Ru(bpy)_2Cl_2$·$2H_2O$] (52 mg, 0.10 mmol) in methanol (20 mL) was added a solution of chlorodiphenylphosphine (44 mg, 0.20 mmol) in methanol (10 mL), and then the mixture was heated at reflux with stirring for 8 h, during which time there was a color change from purple-red to dark purple-red. After the reaction mixture was cooled to room temperature, an excess of KPF_6 (20 mg, 0.11 mmol) was added to the flask and stirred for 30 min. After filtering, the solvent was removed in *vacuo*, and the residue was washed with diethyl ether (2 × 5 mL). Dark purple-red block crystals suitable for X-ray diffraction were obtained by slow evaporation of a mixed dichloromethane-*n*-hexane (1:6) solvent in three days. Yield: 63 mg, 64% (based on ruthenium). – ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.29–8.12 (dd, J = 8.3, 5.4 Hz, 6H, bpy-*H*), 8.03–6.77 (dd, J = 7.8, 6.7 Hz, 6H, bpy-*H*), 7.44–7.31 (m, 10H, PPh_3), 7.17 (m, 4H, bpy-*H*), 3.55 (s,

3H, OCH_3). – ^{31}P NMR (162 MHz, $CDCl_3$, ppm): δ = 45.43 (s, $(CH_3O)PPh_2$). – IR (KBr disc, cm^{-1}): ν(C–N) 1195 (m), ν(C–O) 1054 (m), ν(P–O) 859 (w). – Anal. calc. for $C_{35}H_{33}N_4OCl_5F_6P_2Ru{\cdot}2CH_2Cl_2$: C 42.90, H 3.39; found C 42.92, H 3.38%.

2.6 Synthesis of [Ru(PPh$_3$)Cl$_2$ (κ^3-*N*,*N*,*N*-L1)] (3)

A mixture of $[RuCl_2(PPh_3)_3]$ (96 mg, 0.10 mmol) and **L1** (18 mg, 0.10 mmol) was stirred in tetrahydrofuran (25 mL) for 4 h at room temperature, during which time the color of solution changed from brown to red-brown. After removal of the solvent in *vacuo*, dichloromethane (20 mL) was added and the solution was filtered. The filtrate was concentrated and the residue was washed with diethyl ether (2 × 5 mL) and hexane (2 × 5 mL). Recrystallization from dichloromethane-hexane (1:3) afforded after three days dark red block crystals of (**3**) suitable for X-ray diffraction. Yield: 44 mg, 72% (based on ruthenium). – ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.98 (s, 1H, Ar-*H*), 8.50 (d, *J* = 4.8 Hz, 1H, CH=N), 7.72–7.62 (m, 6H, Ar-*H*), 7.62–7.51 (m, 7H, Ar-*H*), 7.47–7.21 (m, 5H, Ar-*H*), 3.94 (d, *J* = 10.6 Hz, 2H, CH_2), 3.15 (s, 3H, N–CH_3), 2.89 (s, 2H, CH_2), 2.56 (s, 3H, N–CH_3). – ^{31}P NMR (162 MHz, $CDCl_3$, ppm): δ = 29.28 (s, PPh_2). – IR (KBr disc, cm^{-1}): ν(C=N) 1626 (s), ν(C–N) 1182 (m). – Anal. calc. for $C_{28}H_{30}N_3Cl_2PRu$: C 55.00, H 4.95, N 6.87; found C 55.01, H 4.94, N 6.88%.

2.7 Synthesis of [Ru(CO)Cl$_2$ (κ^3-*P*,*N*,*N*-L2)] (4)

To a slurry of $[Ru(CO)_2Cl_2]_n$ (46 mg, 0.20 mmol) in *N*,*N*-dimethylformamide-tetrahydrofuran (1:9, *v*/*v*) (20 mL) was added a solution of **L2** (72 mg, 0.20 mmol) and triethylamine (22 mg, 0.20 mmol) in tetrahydrofuran (5 mL), and then the mixture was heated at 90 °C with stirring overnight, during which time there was a color change from light yellow to yellow. After removal of the solvent in *vacuo*, the residue was washed with diethyl ether (2 × 5 mL) and *n*-hexane (2 × 5 mL). The residue was extracted with dichloromethane (5 mL) and yellow crystals of (**4**) were obtained after layering the filtrate with hexane (15 mL) at room temperature for five days. Yield: 67 mg, 59% (based on ruthenium). – ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.68 (s, 1H, CH=N), 7.72 (d, *J* = 4.0 Hz, 1H, Ar-*H*), 7.66–7.61 (m, 1H, Ar-*H*), 7.54 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.50–7.44 (m, 4H, Ar-*H*), 7.42–7.30 (m, 7H, Ar-*H*), 4.29–4.23 (m, 2H, CH_2), 3.05 (d, *J* = 1.9 Hz, 6H, $N(CH_3)_2$), 2.79–2.75 (m, 2H, CH_2). – ^{31}P NMR (162 MHz, $CDCl_3$, ppm): δ = 58.69 (s, PPh_2). – IR (KBr disc, cm^{-1}): ν(C≡O) 1989 (s), ν(C=N) 1615 (s), ν(C–N) 1225 (s). – Anal. calc. for $C_{24}H_{25}N_2OCl_2PRu$: C 51.44, H 4.50, N 5.00; found C 51.43, H 4.48, N 5.01%.

2.8 X-Ray crystallography

A summary of crystallographic data and experimental details for the ruthenium(II) complexes **1**–**4** is presented in Table 1. Intensity data was collected on a Bruker SMART APEX 2000 CCD diffractometer using graphite-monochromatized Mo*Kα* radiation (λ = 0.71073 Å) at *T* = 296(2) K. The collected frames were processed with the software SAINT [15]. The data was corrected for absorption using the program SADABS [16]. Structures were solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [17, 18]. 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. The dichloromethane molecules in **2** were isotropically refined without hydrogen atoms due to disorder, which resulted in a relatively high *R* value in the final refinement.

CCDC 1991983 (for [(η^6-*p*-cymene)$RuCl_2$(κ^1-*P*-PPh_2OH)] (**1**)), 1991984 (for $[Ru(bpy)_2Cl(\kappa^1\text{-}P\text{-}PPh_2OCH_3)](PF_6)$ (**2**)), 1991985 (for [Ru(PPh_3)Cl_2(κ^3-*N*,*N*,*N*-**L1**)] (**3**)) and 1991986 (for [Ru(CO)Cl_2(κ^3-*P*,*N*,*N*-**L2**)] (**4**)) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

2.9 Catalytic testing

In a typical experiment, a testing tube was filled with acetophenone (1 mmol), KOH in ^{i}PrOH (0.05 mmol KOH in degassed ^{i}PrOH (10 mL)) and the homogeneous catalyst **4** (0.01 mmol). The mixture was stirred at *T* = 70 °C for 10 h under hydrogen atmosphere. After cooling and filtering, the filtrate was diluted with acetone and then analyzed immediately by GC. The conversions are related to the residual unreacted ketone.

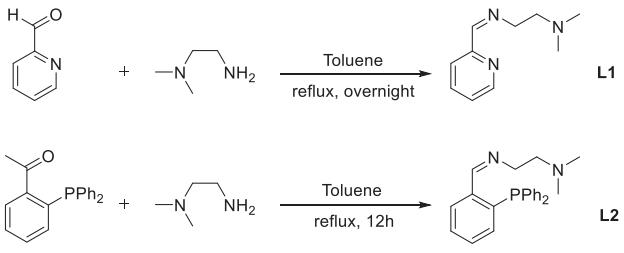
3 Results and discussion

The synthesis of the Schiff base ligands **L1**, **L2** and of the ruthenium(II) complexes **1**–**4** are summarized in

Table 1: Crystallographic data and experimental details for ruthenium(II) complexes [(η^6-*p*-cymene)$RuCl_2$(κ^1-*P*-PPh_2OH)] (**1**), [$Ru(bpy)_2Cl$(κ^1-*P*-PPh_2OCH_3)](PF_6) (**2**), [$Ru(PPh_3)Cl_2$(κ^3-*N*,*N*,*N*-**L1**)] (**3**) and [Ru(CO)Cl_2(κ^3-*P*,*N*,*N*-**L2**)] (**4**).

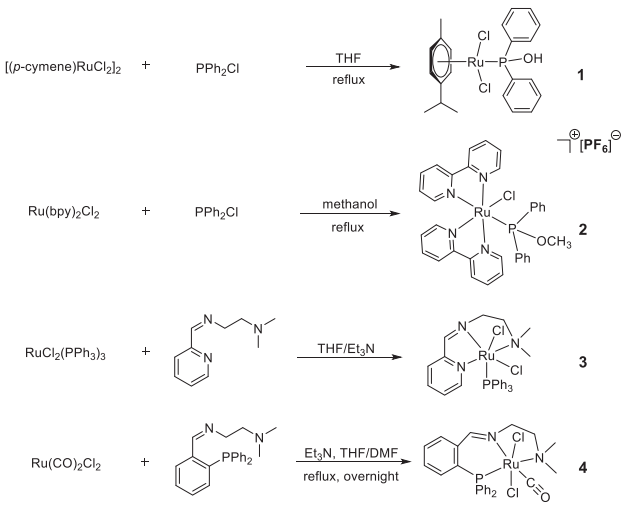
Complex	1	2·2CH_2Cl_2	3	4
Empirical formula	$C_{22}H_{25}Cl_2OPRu$	$C_{35}H_{33}Cl_5F_6N_4OP_2Ru$	$C_{28}H_{30}Cl_2N_3PRu$	$C_{24}H_{25}Cl_2N_2OPRu$
Formula weight	508.36	979.91	611.49	560.40
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$Pca2_1$	$P2_1/n$
a, Å	10.353(5)	18.380(7)	16.113(12)	10.4655(12)
b, Å	12.328(6)	14.395(6)	16.553(13)	12.9050(14)
c, Å	17.518(9)	16.369(7)	10.682(8)	18.119(2)
β, deg	99.465(7)	111.856(6)	90	91.3470(15)
V, Å^3	2205.5(19)	4020(3)	2849(4)	2446.5(5)
Z	4	4	4	4
D_{calc}, g cm^{-3}	1.53	1.62	1.43	1.52
Temperature, K	296(2)	296(2)	296(2)	296(2)
F(000), *e*	1032	1968	1248	1136
μ(Mo*K*α), mm^{-1}	1.0	0.9	0.8	0.9
Total refln	12893	25118	17925	15265
Independent refln	4746	9174	5498	5574
R_{int}	0.0602	0.1009	0.0614	0.0309
Ref. Parameters	248	482	318	282
$R1^a/wR2^b$ ($I > 2\sigma(I)$)	0.0435/0.0783	0.0769/0.1871	0.0399/0.0676	0.0300/0.0646
*R*1/*wR*2 (all data)	0.1091/0.1003	0.1710/0.2459	0.0676/0.0761	0.0443/0.0710
Flack *x*	–	–	−0.06(3)	–
GoF^c	0.972	0.963	0.961	1.039
$\Delta\rho_{fin}$ (max/min), *e* Å^{-3}	0.39/−0.46	0.78/−1.09	0.58/−0.55	0.28/−0.37

$^a R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^b wR2 = \left[\sum w(F_o^2 - F_c^2)2/\sum w(F_o^2)^2\right]^{1/2}$, $w = \left[\sigma^2\left(F_o^2\right) + \left(AP\right)^2 + BP\right]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$ and A and B are constants adjusted by the program. ^{c}GoF = S = $\left[\sum w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})\right]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.



Scheme 1: Synthetic routes to the Schiff base ligands **L1** and **L2**.

Schemes 1 and 2, respectively. The ligands [2-(C_5H_4N)CH=N(CH_2)$_2$N(CH_3)$_2$] (**L1**) and [Ph_2P(*o*-C_6H_4)CH=N(CH_2)$_2$N(CH_3)$_2$] (**L2**) were synthesized from the condensation of *N*,*N*-dimethylethylenediamine with 2-pyridinecarboxaldehyde and 2-(diphenylphosphino)benzaldehyde in toluene, respectively. Treatment of chlorodiphenylphosphine with [(η^6-*p*-cymene)$RuCl_2$]$_2$ and [$Ru(bpy)_2Cl_2$·$2H_2O$] afforded the neutral complex [(η^6-*p*-cymene)$RuCl_2$(κ^1-*P*-PPh_2OH)] (**1**) and the cationic complex [$Ru(bpy)_2Cl$(κ^1-*P*-PPh_2OCH_3)](PF_6) (**2**), respectively, which both have "RuPO" fragments in their molecular structures. Treatment of [$RuCl_2(PPh_3)_3$] with one equiv. **L1** in tetrahydrofuran at room temperature afforded dark red block crystals of [$Ru(PPh_3)Cl_2$(κ^3-*N*,*N*,*N*-**L1**)] (**3**). Two PPh_3 ligands were replaced by one tridentate *N*,*N*′,*N*″-ligand in this reaction. Interaction of [$Ru(CO)_2Cl_2$]$_n$ with one equivalent **L2** in the presence of triethylamine gave a ruthenium(II) complex [Ru(CO)Cl_2(κ^3-*P*,*N*,*N*-**L2**)] (**4**). It is interesting to find that the two chloro ligands were not eliminated in complexes **3** and **4**, and the tridentate **L1** serves as a *N*,*N*′,*N*″-chelating ligand in complex **3**, whereas the tridentate **L2** serves as a *P*,*N*,*N*′-chelating ligand in complex **4**. The IR spectra of the Schiff base ligands **L1**, **L2** and of the complexes **3** and **4** all showed a characteristic band of CH=N groups in the region of 1615–1648 cm^{-1}, which is characteristic of the azomethine group absorptions [19]. In complex **4**, the stretching vibration mode of the terminal C≡O group was found at 1989 cm^{-1}, which is similar to that of other ruthenium carbonyl complexes with phosphine ancillary ligands [$Ru(CO)_2Cl_2$(P∩S] (P∩S = *P*,*S*-chelating diphosphane ligands) (1956–2059 cm^{-1}) [20]. The proton resonance of POH in **1** and of OCH_3 in **2** appeared at δ = 6.62 and 3.55 ppm, respectively, similar to those of ruthenium complexes [$RuCl_2$(η^6-*p*-cymene)(*tert*-BuPhPOH)] (δ = 6.20 ppm) [21] and [Ru_3(μ_3-Se)$_2$(CO)$_7$(P(OMe)Ph_2)$_2$]



Scheme 2: Synthetic routes for the ruthenium(II) complexes **1**–**4**.

(δ = 3.42 and 3.59 ppm), respectively [22]. The ^{31}P NMR spectra of complexes **1** and **2** showed a singlet at 105.7 and 45.43 ppm, respectively, consistent with a *P*-coordinated diphenylphosphinous acid [23].

The structures of ruthenium(II) complexes **1**–**4** have been established by X-ray crystallography. The perspective views of the molecular structures of complexes **1**–**4** are shown in Figures 1–4, with their atom numbering schemes. It should be noted that the structure of complex **1** has been determined before and the conversion of complexed chlorodiphenylphosphine into the PPh_2OH ligand has precedent [21, 24, 25]. This adventitious hydrolysis is an alternative procedure for the synthesis of metal complexes with phosphinous acid PR_2OH ligands (Scheme 3). It is probably due to the high temperature of the reaction and the presence of small amounts of water in the reaction system [26, 27]. The P–O bond lengths are 1.601(3) and 1.617(5) Å in complexes **1** and **2**, respectively, which compare well with those in $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PPh_2(OCH_2CH_2NMe_3))][SbF_6]$ (1.612(2) Å) [28] and $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_6)(PPh_2OH)]$ (1.6040(18) Å) [29]. Complex **2** comprises of one cation $[Ru(bpy)_2Cl(\kappa^1\text{-}P\text{-}PPh_2OCH_3)]^+$, one $[PF_6]^-$ anion, and two CH_2Cl_2 solvent molecules. In the octahedral $[PF_6]^-$ anion, the P–F distances span the range of 1.454(9)–1.563(7) Å. The Ru–N bond lengths are 2.060(6)–2.128(6) Å, together with the bipyridine chelate bite angles of 77.8(2)–78.8(2)°, which compare well with those in $[Ru^{II}(bpy)_2fla][BF_4]$ (fla = flavonolate) (2.023(3)–2.055(3) Å, 79.48(13)–79.51(13)°) [30]. The Ru–P and Ru–Cl bond lengths are 2.285(2) and 2.425(2) Å, respectively, similar to those in complex **1**. In the distorted octahedral coordination sphere of complex **3** bearing tridentate Schiff base ligands, the Ru–N(*N*,*N*-dimethylethylenediamine)

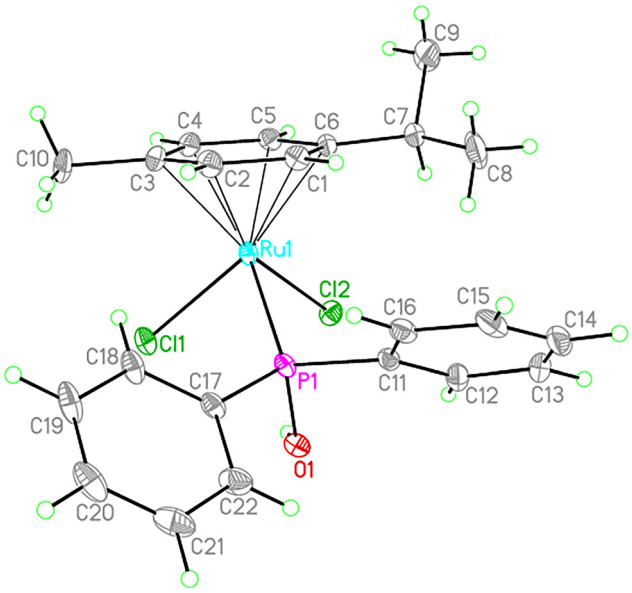


Figure 1: Molecular structure of $[(\eta^6\text{-}p\text{-cymene})RuCl_2(\kappa^1\text{-}P\text{-}PPh_2OH)]$ (**1**) in the crystal. Displacement ellipsoids are shown at the 35% probability level. Selected bond lengths (Å) and angles (deg):Ru(1)–C(1) 2.177(5), Ru(1)–C(2) 2.185(6), Ru(1)–C(3) 2.220(5), Ru(1)–C(4) 2.245(5), Ru(1)–C(5) 2.221(5), Ru(1)–C(6) 2.221(5), Ru(1)–Cl(1) 2.4139(15), Ru(1)–Cl(2) 2.4150(16), Ru(1)–P(1) 2.3087(16), P(1)–O(1) 1.601(3); P(1)–Ru(1)–Cl(1) 83.22(5), P(1)–Ru(1)–Cl(2) 84.38(6), Cl(1)–Ru(1)–Cl(2) 87.29(6), O(1)–P(1)–Ru(1) 113.34(13).

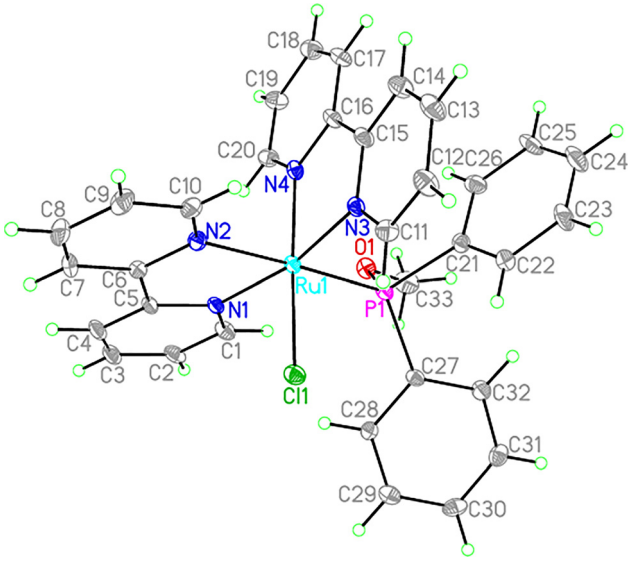


Figure 2: Molecular structure of cations $[Ru(bpy)_2Cl(\kappa^1\text{-}P\text{-}PPh_2OCH_3)]^+$ in crystals of (**2**). The anion is omitted for clarity. Displacement ellipsoids are shown at the 40% probability level. Selected bond lengths (Å) and angles (deg): Ru(1)–N(1) 2.105(6), Ru(1)–N(2) 2.128(6), Ru(1)–N(3) 2.061(6), Ru(1)–N(4) 2.060(6), Ru(1)–P(1) 2.285(2), Ru(1)–Cl(1) 2.425(2), P(1)–O(1) 1.617(5); N(1)–Ru(1)–N(2) 77.8(2), N(4)–Ru(1)–N(3) 78.8(2), N(4)–Ru(1)–N(2) 93.7(2), N(3)–Ru(1)–N(1) 167.9(2), N(2)–Ru(1)–P(1) 176.69(18), N(4)–Ru(1)–Cl(1) 172.74(17), P(1)–Ru(1)–Cl(1) 95.78(8), O(1)–P(1)–Ru(1) 108.4(2).

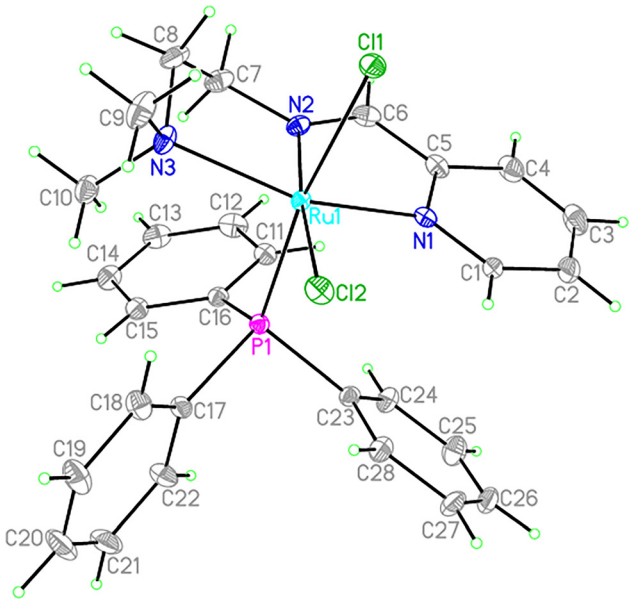


Figure 3: Molecular structure of [Ru(PPh$_3$)Cl$_2$(κ^3-*N*,*N*,*N*-**L1**)] (**3**) in the crystal. Displacement ellipsoids are shown at the 35% probability level. Selected bond lengths (Å) and angles (deg): Ru(1)–N(1) 2.054(4), Ru(1)–N(2) 1.950(4), Ru(1)–N(3) 2.226(4), Ru(1)–P(1) 2.3087(16), Ru(1)–Cl(1) 2.4955(17), Ru(1)–Cl(2) 2.4261(18); N(2)–Ru(1)–N(1) 79.08(16), N(2)–Ru(1)–N(3) 82.26(16), N(1)–Ru(1)–N(3) 160.30(15), Cl(2)–Ru(1)–Cl(1) 86.53(7), P(1)–Ru(1)–Cl(1) 171.93(4), P(1)–Ru(1)–Cl(2) 90.86(7), N(2)–Ru(1)–Cl(2) 172.43(12).

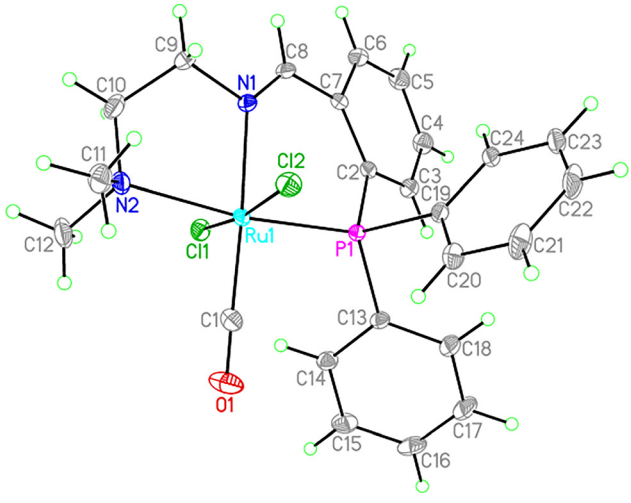
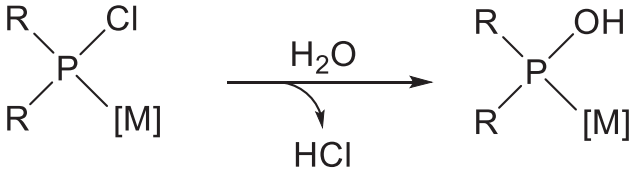


Figure 4: Molecular structure of [Ru(CO)Cl$_2$(κ^3-*P*,*N*,*N*-**L2**)] (**4**) in the crystal. Displacement ellipsoids are shown at the 35% probability level. Selected bond lengths (Å) and angles (deg): Ru(1)–C(1) 1.860(3), Ru(1)–N(1) 2.102(2), Ru(1)–N(2) 2.262(2), Ru(1)–P(1) 2.2718(6), Ru(1)–Cl(1) 2.4122(7), Ru(1)–Cl(2) 2.4038(7); C(1)–Ru(1)–N(1) 177.20(10), C(1)–Ru(1)–N(2) 96.14(10), N(1)–Ru(1)–N(2) 81.06(8), C(1)–Ru(1)–P(1) 92.67(8), N(2)–Ru(1)–P(1) 170.57(6), Cl(2)–Ru(1)–Cl(1) 172.75(2), O(1)–C(1)–Ru(1) 178.7(3), C(1)–Ru(1)–Cl(1) 94.56(8), C(1)–Ru(1)–Cl(2) 92.65(8).



Scheme 3: Alternative procedure to generate complexes with PR_2OH ligands.

bond lengths are 1.950(4) and 2.226(4) Å, together with the *N*,*N*-chelate bite angles of 82.26(16)°, similar to those in complex **4** (2.102(2) and 2.262(2) Å, 81.06(8)°). The average Ru–Cl bond length is 2.461(1) Å in complex **3**, which is a little longer than in the complexes **1** (2.4145(16) Å), **2** (2.425(2) Å) and **4** (2.408(7) Å). In complex **4**, however, the Cl–Ru–Cl bond angle is 172.75(2)°, indicating the *trans*-configuration of the two chloro ligands. The C≡O bond length is 1.111(3) Å and the Ru–C–O bond angle is 178.7(3)°, which are normal for ruthenium(II) carbonyl complexes [31, 32].

Complex [Ru(CO)Cl$_2$(κ^3-*P*,*N*,*N*-**L2**)] (**4**) was selected to explore the catalytic activity, since it has a κ^3-*P*,*N*,*N* Schiff base ligand. Recently, the catalytic hydrogenation of acetophenone by ruthenium(II) complexes containing mixed donor (P^N) ligands has been reported [33, 34]. Under similar conditions, complex **4** gave about 68% conversion, compared with those obtained with pyrazolylphosphite- and pyrazolylphosphinite-ruthenium(II) complexes with P^N ligands (69, 42, 61, 68, 61, 31 and 65%) and the parent complex[Ru(*p*-cymene)Cl$_2$]$_2$ (21%) [33]. The yield was not improved after longer reaction times. In a similar work done by Günnaz and co-workers [35] with tridentate triamine N^N^N-ruthenium(II) complexes, the conversions were from 3 to 73% together with the formation of 2-phenylethanol, which was not observed in the process using **4**, indicating good selectivity of complex **4**. Investigations to understand further the catalytic mechanism are in progress.

In summary, four ruthenium(II) complexes with Ru–Cl functions and substituted Schiff base/phosphine ancillary ligands were synthesized and characterized. Their molecular structures have been determined by single-crystal X-ray crystallography. Ruthenium(II) carbonyl complex **4** with a tridentate κ^3-*P*,*N*,*N* Schiff base ligand exhibited good catalytic performance in the hydrogenation of acetophenone to 1-phenylethanol with good yield and selectivity.

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