



## Note

## Ruthenium(II) complexes with 2-(benzylimino-methyl)-4-R-phenol containing the *trans*(PPh<sub>3</sub>),*cis*(CO,Cl)-{Ru(PPh<sub>3</sub>)<sub>2</sub>(CO)Cl}<sup>+</sup> unit

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## ABSTRACT

Reactions of [Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>] with 2-(benzylimino-methyl)-4-R-phenol (H<sup>R</sup>L, R = H, Cl, Br and OMe) in boiling methanol in presence of triethylamine afford ruthenium(II) complexes of general formula [Ru(<sup>R</sup>L)(PPh<sub>3</sub>)<sub>2</sub>(CO)Cl] in 57–64% yield. Microanalysis, spectroscopic (infrared, electronic and NMR) and cyclic voltammetric measurements have been used for the characterization of the complexes. Crystal structures of two representative complexes have been determined by X-ray crystallography. The carbonyl, the chloride, the N,O-donor <sup>R</sup>L<sup>−</sup> and the two mutually *trans* PPh<sub>3</sub> molecules assemble a distorted octahedral CCINOP<sub>2</sub> coordination sphere around the metal centre in each complex. The complexes display the Ru(II) → Ru(III) oxidation in the potential range 0.62–1.16 V (vs. Ag/AgCl).

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## 1. Introduction

In majority of the organometallic complexes of ruthenium, the oxidation state of the metal centre is +2 [1–4]. Among the few known ruthenium(III) complexes containing the M–C bond [5–15], the cyclo-metallated species are particularly scarce [12–15]. Recently we have demonstrated that the Schiff bases (H<sub>2</sub>L) derived from various acid hydrazides and benzaldehyde or acetophenone are very efficient in producing cyclo-metallated ruthenium(III) complexes [16,17]. Reaction of H<sub>2</sub>L, [Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>] and N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (1:1:2 mole ratio) in methanol under aerobic condition leads to the facile formation of *trans*-[Ru(L)(PPh<sub>3</sub>)<sub>2</sub>Cl] where L<sup>2−</sup> acts as C,N,O-donor. In our attempts to synthesize similar *ortho*-metallated ruthenium(III) species we have treated a mixture of 2-(benzylimino-methyl)-4-R-phenol (H<sup>R</sup>L, R = H, Cl, Br and OMe) and N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> with [Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>] in methanol in presence of air. However, instead of the *ortho*-metallated ruthenium(III) complexes bivalent ruthenium complexes of molecular formula [Ru(<sup>R</sup>L)(PPh<sub>3</sub>)<sub>2</sub>(CO)Cl] have been obtained. Herein we describe the synthesis, characterization and the redox properties of these complexes. X-ray structures of two representative complexes are also reported.

## 2. Experimental

## 2.1. Materials

The Schiff bases (H<sup>R</sup>L) were prepared in 70–75% yields by condensation reactions of equimolar amounts of benzylamine and the corresponding 5-R-salicylaldehyde in methanol [14]. [Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>] was prepared by following a reported procedure [18]. All other chemicals and solvents were of analytical grade available commercially and were used without further purification.

## 2.2. Physical measurements

A Thermo Finnigan Flash EA1112 series elemental analyzer was used to collect the microanalytical (C, H, N) data. Room temperature (298 K) magnetic susceptibilities were measured using a Sherwood Scientific balance. Solution electrical conductivities were measured with a Digisun DI-909 conductivity meter. Infrared spectra were collected on a Nicolet 5700 FT-IR spectrophotometer. A Cary 100 Bio UV/vis spectrophotometer was used to record the electronic spectra. The <sup>1</sup>H (Si(CH<sub>3</sub>)<sub>4</sub> as internal standard) NMR spectra were collected with the help of a Bruker 400 MHz NMR spectrometer. Cyclic voltammetric experiments with dichloromethane solutions of the complexes containing tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte were performed with the help of a CH-Instruments model

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620A electrochemical analyzer. The three electrode measurements were carried out at 298 K under dinitrogen atmosphere with a platinum disk working electrode, a platinum wire auxiliary electrode and an Ag/AgCl reference electrode. Under identical condition the  $\text{Fc}^+/\text{Fc}$  couple was observed at 0.65 V. The potentials reported in this work are uncorrected for junction contributions.

### 2.3. Synthesis of $[\text{Ru}^{\text{H}}\text{L}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$ (**1**)

Solid  $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$  (195 mg, 0.20 mmol) was added to a methanol solution (30 ml) of  $\text{H}^{\text{H}}\text{L}$  (43 mg, 0.20 mmol) and  $\text{N}(\text{C}_2\text{H}_5)_3$  (0.06 ml, 44 mg, 0.43 mmol) and the mixture was boiled under reflux for 5 h. The solid obtained after cooling to room temperature was collected by filtration, washed thoroughly with *n*-hexane and dried in air. This solid was dissolved in minimum amount of dichloromethane and transferred to a neutral aluminium oxide column. The first moving light yellow band was eluted with dichloromethane and discarded. The second brownish yellow band containing the complex was eluted with dichloromethane containing 5% acetone. Recrystallization of the complex was performed from dichloromethane–hexane (1:1) mixture. Yield: 105 mg (58%). *Anal. Calc.* for  $\text{RuC}_{51}\text{H}_{42}\text{NO}_2\text{P}_2\text{Cl}$ : C, 68.11; H, 4.71; N, 1.56. Found: C, 67.84; H, 4.53; N, 1.38%. UV–vis in  $\text{CH}_2\text{Cl}_2$  ( $\lambda$  (nm) ( $\epsilon$  ( $\text{M}^{-1}\text{cm}^{-1}$ ))): 418 (4190), 358 (8650), 294 sh (11800).  $E_{\text{pa}}$  (V): 0.68.

The other three complexes having the same general formula  $[\text{Ru}^{\text{R}}\text{L}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$  (**2** (R = Cl), **3** (R = Br) and **4** (R = OMe)) were synthesized from  $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$ , the corresponding Schiff base ( $\text{H}^{\text{R}}\text{L}$ ) and  $\text{N}(\text{C}_2\text{H}_5)_3$  in 60–64% yields by following procedures very similar to that described above for **1** (R = H). *Anal. Calc.* for  $\text{RuC}_{51}\text{H}_{41}\text{NO}_2\text{P}_2\text{Cl}_2$  (**2**): C, 65.60; H, 4.43; N, 1.50. Found: C, 65.49; H, 4.37; N, 1.36%. UV–vis in  $\text{CH}_2\text{Cl}_2$  ( $\lambda$  (nm) ( $\epsilon$  ( $\text{M}^{-1}\text{cm}^{-1}$ ))): 424 (2200), 348 (8150), 295 sh (12300).  $E_{\text{pa}}$  (V): 0.81. *Anal. Calc.* for  $\text{RuC}_{51}\text{H}_{41}\text{NO}_2\text{P}_2\text{ClBr}$  (**3**): C, 62.62; H, 4.22; N, 1.43. Found: C, 62.28; H, 4.01; N, 1.22%. UV–vis in  $\text{CH}_2\text{Cl}_2$  ( $\lambda$  (nm) ( $\epsilon$  ( $\text{M}^{-1}\text{cm}^{-1}$ ))): 416 (3100), 340 (6960), 270 sh (38600).  $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$  (V) ( $\Delta E_{\text{p}} = E_{\text{pa}} - E_{\text{pc}}$  (mV)): 1.16 (110). *Anal. Calc.* for  $\text{RuC}_{52}\text{H}_{44}\text{NO}_3\text{P}_2\text{Cl}$  (**4**): C, 67.20; H, 4.77; N, 1.51. Found: C, 66.97; H, 4.61; N, 1.40%. UV–vis in  $\text{CH}_2\text{Cl}_2$  ( $\lambda$  (nm) ( $\epsilon$  ( $\text{M}^{-1}\text{cm}^{-1}$ ))): 434 (2200), 353 (6350), 298 sh (10100).  $E_{\text{pa}}$  (V): 0.62.

### 2.4. X-ray crystallography

Complexes **2** and **3** crystallize as **2**·CH<sub>3</sub>CN and **3**·CH<sub>3</sub>CN in the space group *C2/c* from acetonitrile solution. For both crystals, unit cell parameters and the intensity data at 298 K were obtained on a Bruker-Nonius SMART APEX CCD single crystal diffractometer, equipped with a graphite monochromator and a Mo K $\alpha$  fine-focus sealed tube ( $\lambda = 0.71073$  Å). The SMART software was used for data acquisition and the SAINT-PLUS software was used for data extraction [19]. The data were corrected for absorption with the help of SADABS program [20]. Both structures were solved by direct methods and refined on  $F^2$  by full-matrix least-squares procedures. In each case, the asymmetric unit contains one complex molecule and one acetonitrile molecule. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model. The SHELX-97 programs [21] were used for structure solution and refinement. The ORTEK6a [22] and PLATON packages [23] were used for molecular graphics. Selected crystal data are listed in Table 1.

## 3. Results and discussion

In boiling methanol, reactions of 2-(benzylimino-methyl)-4-R-phenol ( $\text{H}^{\text{R}}\text{L}$ , R = H, Cl, Br and OMe),  $\text{N}(\text{C}_2\text{H}_5)_3$  and  $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$

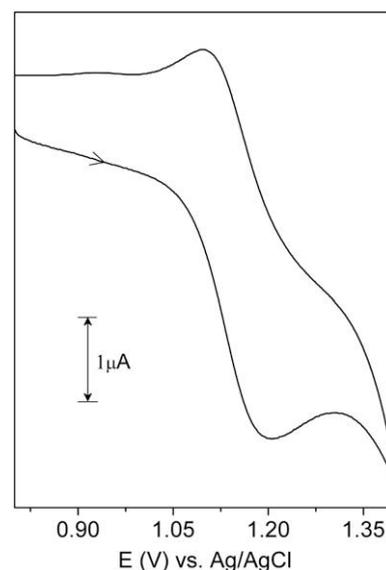
**Table 1**

Crystal data for  $[\text{Ru}^{\text{Cl}}\text{L}(\text{PPh}_3)_2(\text{CO})\text{Cl}] \cdot \text{CH}_3\text{CN}$  (**2**·CH<sub>3</sub>CN) and  $[\text{Ru}^{\text{Br}}\text{L}(\text{PPh}_3)_2(\text{CO})\text{Cl}] \cdot \text{CH}_3\text{CN}$  (**3**·CH<sub>3</sub>CN).

Complex	<b>2</b> ·CH <sub>3</sub> CN	<b>3</b> ·CH <sub>3</sub> CN
Chemical formula	$\text{RuC}_{53}\text{H}_{44}\text{N}_2\text{O}_2\text{Cl}_2\text{P}_2$	$\text{RuC}_{53}\text{H}_{44}\text{N}_2\text{O}_2\text{ClBrP}_2$
Formula weight	974.87	1019.27
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> (Å)	20.877(4)	21.031(3)
<i>b</i> (Å)	12.466(3)	12.4573(16)
<i>c</i> (Å)	35.548(7)	35.479(4)
$\beta$ (°)	90.822(4)	91.647(2)
<i>V</i> (Å <sup>3</sup> )	9251(3)	9291(2)
<i>Z</i>	8	8
$\rho$ (g cm <sup>-3</sup> )	1.400	1.457
$\mu$ (mm <sup>-1</sup> )	0.567	1.367
Reflections collected	51842	52189
Reflections unique	10590	10594
Reflections [ $I \geq 2\sigma(I)$ ]	8582	7605
Parameters	560	560
$R_1, wR_2$ [ $I \geq 2\sigma(I)$ ]	0.0708, 0.1361	0.0489, 0.1114
$R_1, wR_2$ [all data]	0.0925, 0.1440	0.0764, 0.1215
Goodness-of-fit on $F^2$	1.072	1.041
Largest difference in peak and hole (e Å <sup>-3</sup> )	1.072, -0.752	0.904, -0.467

in 1:2:1 mole ratio under aerobic condition result into the formation of ruthenium(II) complexes  $[\text{Ru}^{\text{R}}\text{L}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$  (**1** (R = H), **2** (R = Cl), **3** (R = Br) and **4** (R = OMe)) in 58–64% yields. The elemental (C, H, N) analysis data for the complexes are consistent with the above general formula. The solvent methanol used during the synthesis is in all likelihood the source of the carbonyl in these complexes [16]. The diamagnetic nature of **1–4** confirms the +2 oxidation state and the low-spin character of the metal centre in each complex. All the complexes behave as non-electrolyte in solution. It may be noted that in boiling ethanol the reaction of  $\text{H}^{\text{R}}\text{L}$  (R = H) with  $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$  in 2:1 mole ratio is known to afford *trans*- $[\text{Ru}^{\text{II}}(\text{H}^{\text{R}}\text{L})_2(\text{PPh}_3)_2]$  and  $[\text{Ru}^{\text{III}}(\text{H}^{\text{R}}\text{L})(\text{H}^{\text{R}}\text{L}^-)(\text{PPh}_3)]$  where  $\text{H}^{\text{R}}\text{L}^-$  is N,O-donor and  $\text{H}^{\text{R}}\text{L}^{2-}$  is C,N,O-donor [14].

Infrared spectra of **1–4** in KBr display a strong band in the range 1914–1919 cm<sup>-1</sup>. This band is attributed to the metal coordinated carbonyl group [24]. The origin of the medium intensity band observed within 1624–1630 cm<sup>-1</sup> is most likely due to the C=N stretch of the ligand ( $\text{R}^{\text{L}}\text{L}^-$ ) [25–30]. In all the spectra three strong



**Fig. 1.** Cyclic voltammogram (scan rate 50 mV s<sup>-1</sup>) of  $[\text{Ru}^{\text{Br}}\text{L}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$  (**3**) in dichloromethane (0.1 M TBAP) at 298 K.

bands are observed at  $\sim 745$ ,  $\sim 696$  and  $\sim 515$   $\text{cm}^{-1}$ . Such bands are common for complexes of the *trans*- $\{\text{Ru}(\text{PPh}_3)_2\}$  moiety [14,16,17,27–30].

Electronic spectra of **1–4** were collected using their dichloromethane solutions. The spectral profiles of the four complexes are very similar. They display three strong absorptions in the

**Table 2**

Selected bond lengths (Å) and bond angles ( $^\circ$ ) for  $[\text{Ru}^{\text{C}^{\text{L}}}\text{L}(\text{PPh}_3)_2(\text{CO})\text{Cl}]\cdot\text{CH}_3\text{CN}$  (**2**· $\text{CH}_3\text{CN}$ ) and  $[\text{Ru}^{\text{Br}^{\text{L}}}\text{L}(\text{PPh}_3)_2(\text{CO})\text{Cl}]\cdot\text{CH}_3\text{CN}$  (**3**· $\text{CH}_3\text{CN}$ ).

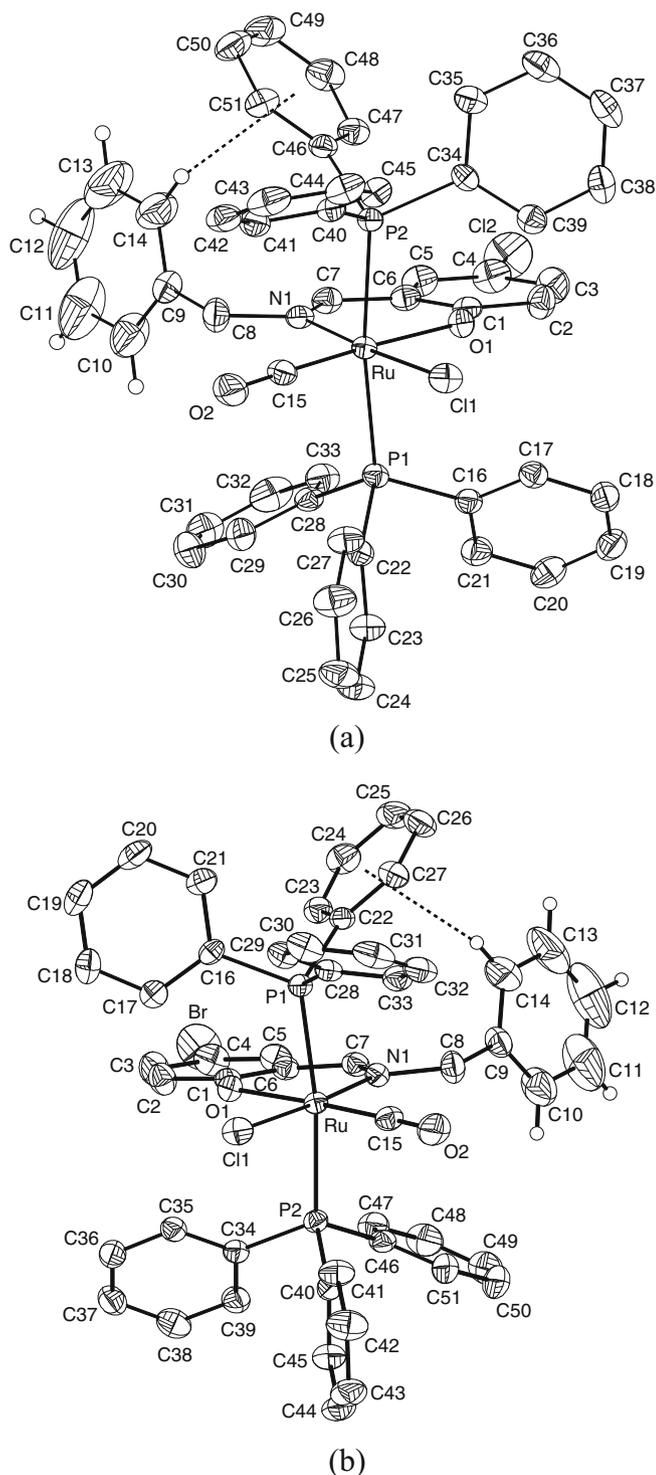
Parameter	<b>2</b> · $\text{CH}_3\text{CN}$	<b>3</b> · $\text{CH}_3\text{CN}$
Ru–O(1)	2.067(3)	2.068(2)
Ru–N(1)	2.083(3)	2.073(3)
Ru–Cl(1)	2.4400(12)	2.4329(9)
Ru–C(15)	1.828(4)	1.840(3)
Ru–P(1)	2.4039(11)	2.4180(9)
Ru–P(2)	2.4186(11)	2.4005(9)
C(15)–O(2)	1.153(5)	1.146(4)
O(1)–Ru–N(1)	89.17(12)	88.78(9)
O(1)–Ru–Cl(1)	87.95(8)	87.95(6)
O(1)–Ru–C(15)	176.51(15)	176.91(12)
O(1)–Ru–P(1)	87.71(8)	86.50(6)
O(1)–Ru–P(2)	86.72(8)	87.94(6)
N(1)–Ru–Cl(1)	176.56(9)	176.25(7)
N(1)–Ru–C(15)	94.22(16)	94.19(13)
N(1)–Ru–P(1)	91.83(9)	92.80(7)
N(1)–Ru–P(2)	92.89(9)	91.70(7)
Cl(1)–Ru–C(15)	88.68(14)	89.11(11)
Cl(1)–Ru–P(1)	89.94(3)	85.17(3)
Cl(1)–Ru–P(2)	85.06(4)	90.02(3)
C(15)–Ru–P(1)	91.38(13)	94.22(10)
C(15)–Ru–P(2)	93.89(13)	91.09(10)
P(1)–Ru–P(2)	172.65(4)	172.77(3)
Ru–C(15)–O(2)	178.7(4)	178.3(3)

wavelength ranges 416–434, 340–358 and 270–298 nm due to metal-to-ligand charge transfer and ligand centred transitions.

Proton NMR spectra of **1–4** in  $\text{CDCl}_3$  display the methylene protons of  $^{\text{R}^{\text{L}}}$  as a singlet within 4.34–4.40 ppm. A broad weak signal observed in the range 8.38–8.45 is perhaps associated with the metal coordinated azomethine proton. The aromatic protons appear as complex multiplets within 7.0–7.9 ppm. The methyl protons of the methoxy substituent on the ligand in **4** resonate as a singlet at 3.53 ppm.

The cyclic voltammograms of **1–4** display a metal centred oxidation in the potential range 0.62–1.16 V. Except for **3**, the oxidation is irreversible for the remaining three complexes. In the case of **3** also the cathodic peak current is smaller than the anodic peak current (Fig. 1). The trend in the potential values indicates that the oxidation of the metal centre becomes more difficult as the substituent on  $^{\text{R}^{\text{L}}}$  becomes more electron withdrawing. Thus the potential is highest for  $\text{R} = \text{Br}$  and it is lowest for  $\text{R} = \text{OMe}$ .

Molecular structures of complexes **2** and **3** determined by X-ray crystallography are shown in Fig. 2. Selected bond parameters for both complexes are listed in Table 2. The metal centre is in distorted octahedral  $\text{CCINOP}_2$  coordination sphere in each complex. The N,O-donor  $^{\text{R}^{\text{L}}}$ , the carbonyl C-atom and the chloride form a CCINO square plane around the metal centre and the two  $\text{PPh}_3$  molecules occupy the axial positions. The *cis* and *trans* bond angles are in the ranges  $85.06(4)$ – $94.22(16)^\circ$  and  $172.65(4)$ – $176.91(12)^\circ$ , respectively. The Ru–O(phenolate), the Ru–N(imine), the Ru–Cl and the *trans* Ru–P bond lengths are comparable with the bond lengths observed in ruthenium(II) complexes having the same coordinating atoms [27,31–37]. The Ru–C and the C–O bond lengths and the Ru–C–O bond angle are within the range reported for carbonyl coordinated ruthenium(II) species [35–39]. In each of the two molecules, one *ortho*-C–H of the benzyl phenyl ring is directed towards the centroid (Cg) of a phenyl ring of one of the  $\text{PPh}_3$  ligands (Fig. 2). In **2**, the H···Cg and C–H···Cg distances and the C–H···Cg angle are 2.80 and 3.695(7) Å and  $163^\circ$ , respectively. The corresponding values for **3** are 2.79 and 3.698(6) Å and  $165^\circ$ , respectively. These parameters clearly indicate an intramolecular C–H··· $\pi$  interaction in both **2** and **3** [40].



**Fig. 2.** Molecular structures of (a)  $[\text{Ru}^{\text{C}^{\text{L}}}\text{L}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$  (**2**) and (b)  $[\text{Ru}^{\text{Br}^{\text{L}}}\text{L}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$  (**3**) with the atom labeling schemes. All non-hydrogen atoms are represented by their 30% probability thermal ellipsoids. Except for the benzyl group phenyl ring of  $^{\text{R}^{\text{L}}}$ , all other hydrogen atoms are omitted for clarity.

#### 4. Conclusion

Synthesis and physical properties of four new ruthenium(II) complexes *trans*(PPh<sub>3</sub>),*cis*(CO,Cl)-[Ru(<sup>R</sup>L)(PPh<sub>3</sub>)<sub>2</sub>(CO)Cl] (<sup>R</sup>L, 2-(benzylimino-methyl)-4-R-phenol (R = H, Cl, Br and OMe)) are described. In methanol, reactions of H<sup>R</sup>L, N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> and [Ru(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] in 1:2:1 mole ratio under reflux condition afford these complexes in good yield. Originally these reactions were performed in search of ruthenium(III) complexes, *trans*-[Ru(<sup>R</sup>L')(PPh<sub>3</sub>)<sub>2</sub>Cl], where <sup>R</sup>L'<sup>2-</sup> is expected to act as C,N,O-donor ligand due to *ortho*-metallation at the benzyl group phenyl ring. Molecular structures of [Ru(<sup>Cl</sup>L)(PPh<sub>3</sub>)<sub>2</sub>(CO)Cl] and [Ru(<sup>Br</sup>L)(PPh<sub>3</sub>)<sub>2</sub>(CO)Cl] determined by X-ray crystallography reveal an intramolecular C–H... $\pi$  interaction involving the *ortho*-C–H of the benzyl group phenyl ring of <sup>R</sup>L<sup>-</sup> and a phenyl ring of PPh<sub>3</sub>. Perhaps this interaction plays an important role in the formation of the present series of complexes in preference to the targeted *ortho*-metallated ruthenium(III) species.

#### 5. Supplementary material

CCDC 751460 and 751461 contains the supplementary crystallographic data for **2**-CH<sub>3</sub>CN and **3**-CH<sub>3</sub>CN. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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