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Ru(0)-azoimine-carbonyl and Ru(II)-pyridyl-azo-imidazole complexes

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Abstract

The reaction of 2-(3′-pyridylazo)imidazole (3′-PyaiH) or its 1-alkyl derivative, 3′-PyaiR, with $Ru(CO)_3(PPh_3)_2$ has synthesized air stable, moisture insensitive, diamagnetic Ru(0) complexes, $[Ru(CO)(3'\text{-PyaiR})(PPh_3)_2]$. The ligands serve as an unsymmetric N,N′-chelating agent (N(imidazole) and N(azo) are abbreviated as N and N′, respectively). The X-ray structure determination of $[Ru(CO)(3'\text{-PyaiH})(PPh_3)_2]$ shows a square pyramidal geometry. The square plane is made up of Ru, 2P, C(O), N(1), and with N(3) at the apex. Other spectroscopic studies (IR, UV–Vis, NMR) support the stereochemistry. Electrochemistry shows three consecutive anodic peaks (E_{pa}) and suggest irreversible redox responses of Ru(I)/Ru(0), Ru(II)/Ru(I), Ru(III)/Ru(II) and azo reductions. Oxidation by Cl_2 of $[Ru(CO)(3'\text{-PyaiR})(PPh_3)_2]$ has isolated the Ru(II)-complex as the perchlorate salt, $[Ru(CO)(Cl)(3'\text{-PyaiR})(PPh_3)_2](ClO_4)$. A solution of $RuCl_3$ and 3′-PyaiR in ethanol has isolated two isomers of the composition $Ru(3'\text{-PyaiR})_2Cl_2$. They have been characterized by spectral and electrochemical data.

Keywords: Pyridylazoimidazoles; Ru(0)-azoimine-carbonyl; Cl_2-oxidation; X-ray crystal structure; Electrochemistry; Coordination compounds

1. Introduction

Ruthenium chemistry of heterocyclic nitrogenous ligands has developed in different dimensions primarily due to their valence isomerism, different chemical, photophysical, photochemical, catalytic and redox activities [1–12]. The major work has grown around polypyridine bases. The number of hetero-atoms, ring size and the substituents in the heterocyclic ring significantly modify the π-acidity and regulate the physical and chemical properties of the compounds [13]. In this respect, the design of the ligand on the heterocyclic backbone, in general, and pyridine, in particular, to gain control over the structure and reactivity of the complexes has gained momentum. However, the majority of the work has been focused on preparing α-diimine (–N=C–C=N–) derivatives.

Our interest lies in the design of heterocyclic azo compounds, those bearing the chelated azoimine, –N=N–C=N–, function which is isoelectronic with the diimine group (–N=C–C=N–) [14]. The presence of the azo group enhances the π-acidity of the function and is responsible for photochromic, pH – responsive and redox activity to the molecules. For the last few years we have been engaged in the development of the transition metal chemistry of arylazoimidazoles [14–20]. Imidazole was chosen because of its chemical and biological ubiquity. Our present program is to design mixed heterocyclic azo compounds and to explore their metal complexes. There are reports on biheterocyclic azo ligands (**1**) in which two the same heterocycles, like pyridine (Py), bipyridine (bpy), 1,10-phenanthroline (phen) are bridged by a –N=N– group [21–24] (Scheme 1). However, mixed heterocyclic azo compounds (**2**) are scarce [25]. We have reported for the first time a mixed biheterocyclic azo compound [26] in which imidazole, a five membered heterocycle, is bridged to pyridine, a six membered heterocycle, by a –N=N– function (**3**). Ruthenium complexes of arylazo heterocycles have been reported by us [13–20,26] and others [4–12,21–25,27]. In this paper we report the reaction of 3′-PyaiR (**3**) with

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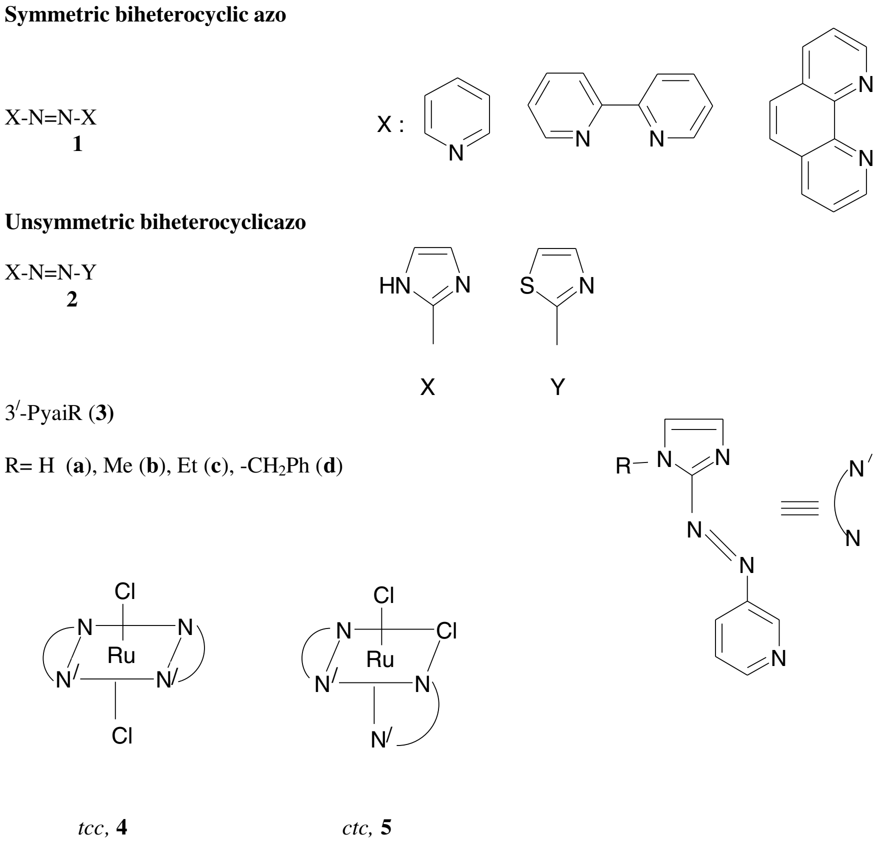

Scheme 1.

ruthenium trichloride and ruthenium phosphine carbonyl compounds, $Ru(CO)_3(PPh_3)_2$. The structure in one case has been confirmed by X-ray diffraction study.

2. Result and discussion

2.1. Ruthenium(II) coordination complexes and their isomer characterisation

2-(3′-Pyridylazo)imidazole (3′-PyaiH, **3a**) and 1-alkyl-2-(3′-pyridylazo)imidazoles (3′-PyaiR: R = Me (**3b**), Et (**3c**), CH_2Ph (**3d**)) have been used in the synthesis of coordination complexes of ruthenium(II). An ethanolic solution of 3′-PyaiR reacts with $RuCl_3$ under dinitrogen and affords the complexes, $Ru(3'\text{-PyaiR})_2Cl_2$ (**4**,**5**) via spontaneous reductive chelation (Eq. (1)). Dark colored crystalline compounds are collected from the cold solution. Two isomers, green and blue-violet have been separated from the mixture by chromatographic separation. The pseudo-octahedral complexes of the formula, $Ru(N,N')_2Cl_2$ with unsymmetric chelating ligands may exist in five geometrically isomeric forms [14]. The isomers are assigned in terms of sequences of coordination of pairs of Cl; N(imidazole) and N(azo): two isomers *trans–trans–trans* and *trans–cis–cis* belong to *trans*-$RuCl_2$ and three isomers *cis–trans–cis*, *cis–cis–trans* and *cis–cis–cis* belong to *cis*-$RuCl_2$ configurations. In this case the green (**4**) and blue-violet (**5**) complexes are assigned to *trans–cis–cis* (tcc) and *cis–trans–cis* (ctc) $Ru(3'\text{-PyaiR})_2Cl_2$. The complexes are diamagnetic (t_{2g}^6) and non-conducting. The microanalytical data support their composition. The spectroscopic data determine the structure of these complexes. The reaction between 3′-PyaiH and $RuCl_3$ in refluxing ethanol under a N_2 environment has separated dark coloured insoluble compounds. Because of the insolubility of the complexes we would not proceed further to identify the compounds.

$$RuCl_3 + 2\,3'\text{-PyaiR} \xrightarrow{\text{EtOH/boil}} Ru(3'\text{-PyaiR})_2Cl_2 + Cl^- \qquad (1)$$

Infrared spectra of the free ligands and complexes were compared to assign the major frequencies. The complexes exhibit stretching frequencies ν(N=N) and ν(C=N) at 1370–1380 and 1550–1580 cm^{-1}, respectively, and ν(N=N) has been shifted to shorter wavelength by 10–15 cm^{-1} compared to the free ligand value. The green isomers (**4**) display a single ν(Ru–Cl) stretch at 320–325 cm^{-1}; blue-violet isomers (**5**) exhibit two stretches at 310–315 and 320–325 cm^{-1}. These values support the *trans*-$RuCl_2$ and *cis*-$RuCl_2$ configuration of **4** and **5**, respectively. We have not been attempted to assign all other stretches; however they are shifted to higher frequency compared to free ligand spectra.

The electronic spectral data were collected in MeCN (Table 1, Fig. 1). The transitions <400 nm are of the intra-ligand charge transfer type and are not considered

Table 1
UV–Vis spectral[a] and cyclic voltammetric[b] data of the ruthenium complexes

Compounds	λ_{max}, nm ($10^{-3}\varepsilon$, M^{-1} cm^{-1})	Metal oxidation Ru(III)/Ru(II)	Ligand reduction
tcc-Ru(3′-PyaiMe)$_2$Cl$_2$ (**4b**)	644 (1.82), 364 (10.61)	0.724 (90)	−0.651 (100), −0.851 (120), −1.28[d]
tcc-Ru(3′-PyaiEt)$_2$Cl$_2$ (**4c**)	662 (6.29), 392 (8.47), 344 (11.36)	0.812 (100)	−0.635 (120), −0.825 (120), −1.26[d]
tcc-Ru(3′-PyaiBz)$_2$Cl$_2$ (**4d**)	660 (6.18), 390 (10.44), 330 (12.30)	0.75 (100)	−0.642 (100), −0.835 (100), −1.25[d]
ctc-Ru(3′-PyaiMe)$_2$Cl$_2$ (**5b**)	556 (3.34), 366 (10.01)	0.845 (120)	−0.622 (100), −0.818 (120), −1.27[d]
ctc-Ru(3′-PyaiEt)$_2$Cl$_2$ (**5c**)	554 (7.70), 376 (26.04), 358 (22.75)	0.768 (100)	−0.618 (110), −0.800 (120), −1.25[d]
ctc-Ru(3′-PyaiBz)$_2$Cl$_2$ (**5d**)	552 (2.85), 366 (9.04)	0.865 (120)	−0.600 (100), −0.805 (100), −1.24[d]
Ru(3′-PyaiH)(CO)(PPh$_3$)$_2$ (**6a**)	472 (8.25), 376 (6.06), 340 (5.47)	1.20[c]	−0.75 (120), −0.91 (140)
Ru(3′-PyaiMe)(CO)(PPh$_3$)$_2$ (**6b**)	478 (7.14), 374 (18.15), 362 (17.52)	1.28[c]	−0.729 (110), −0.85 (100)
Ru(3′-PyaiEt)(CO)(PPh$_3$)$_2$ (**6c**)	472 (3.44), 384 (8.58)	1.32[c]	−0.72 (120), −0.80 (100)
Ru(3′-PyaiBz)(CO)(PPh$_3$)$_2$ (**6d**)	472 (4.24), 374 (18.35), 360 (17.58)	1.15[c]	−0.74 (140), −1.10 (140)
[Ru(3′-PyaiH)(CO)(Cl)(PPh$_3$)$_2$](ClO$_4$) (**7a**)	506 (10.25), 388 (9.76)	0.785 (130)	−0.610 (120), −0.821 (140)
[Ru(3′-PyaiMe)(CO)(Cl)(PPh$_3$)$_2$](ClO$_4$) (**7b**)	516 (11.99), 398 (11.36), 280 (19.70)	0.778 (120)	−0.628 (130), −0.798 (140)
[Ru(3′-PyaiEt)(CO)(Cl)(PPh$_3$)$_2$](ClO$_4$) (**7c**)	504 (8.53), 384 (7.35)	0.770 (130)	−0.620 (130), −0.804 (160)
[Ru(3′-PyaiBz)(CO)(Cl)(PPh$_3$)$_2$](ClO$_4$) (**7d**)	506 (9.25), 386 (8.16)	0.788 (120)	−0.610 (120), −0.815 (140)

[a] Solvent: CH$_3$CN.

[b] Solvent: MeCN, platinum disk milli electrode, SCE reference, [Bu$_4$N][ClO$_4$] supporting electrolyte, scan rate 50 mV s^{-1}. Potentials are expressed in V, $E_{1/2}$, $\Delta E_p = |E_{pa} - E_{pc}|$, mV.

[c] E_{pa} (anodic peak potential).

[d] E_{pc} (cathodic peak potential).

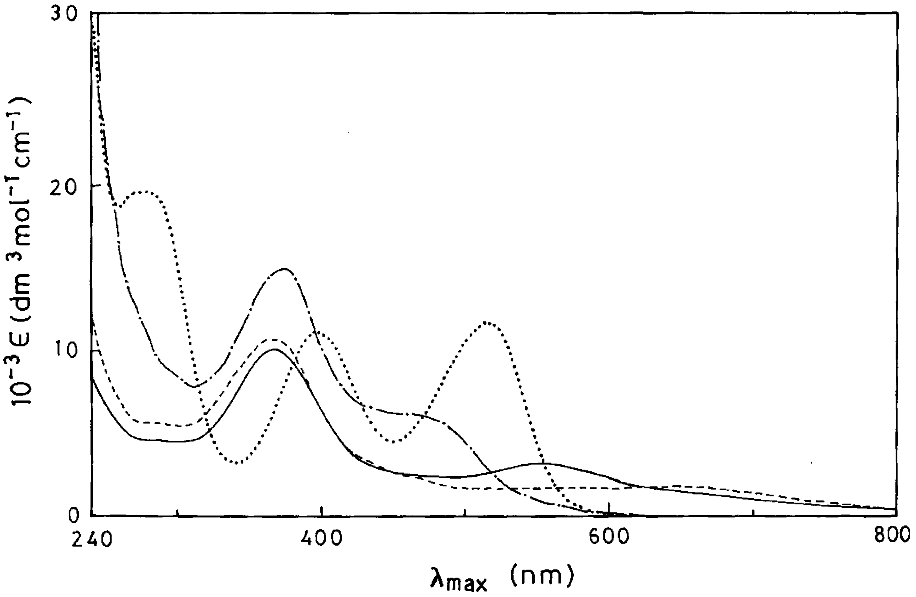

Fig. 1. UV–Vis spectra of ctc-Ru(3′-PyaiMe)$_2$Cl$_2$ (**5b**) (—); tcc-Ru(3′-PyaiMe)$_2$Cl$_2$ (**4b**) (---); Ru(3′-PyaiMe)(CO)(PPh$_3$)$_2$ (**6b**) (—·—·—); [Ru(3′-PyaiMe)(CO)(Cl)(PPh$_3$)$_2$](ClO$_4$) (**7b**) (· · ·).

further. *tcc*-Ru(3′-PyaiR)$_2$Cl$_2$ (**4**) show high intense transitions ($\varepsilon \sim 10^4$ dm^3 mol^{-1} cm^{-1}) in the region 640–660 nm while the blue-violet isomers, ctc-Ru(3′-PyaiR)$_2$Cl$_2$ (**5**) give transitions at higher energies 550–560 nm (Fig. 2). These are assigned to the MLCT transitions.

The stereochemistry of the complexes is supported by ^{1}H NMR spectral data (Table 2) collected in CDCl$_3$. The signals were assigned on the basis of the spin–spin interaction and on comparing with free ligand values. The N(1)–R signals are as follows. The N–Me signal appears at 4.2 and 4.1 ppm in the green (**4a**) and blue-violet (**5a**) complexes, respectively. The methylene, –N–CH$_2$–(CH$_3$) appears as a quartet at 4.4 ppm (^2J, 10.0 Hz) and the methyl, (–N–CH$_2$)–CH$_3$ shows a triplet signal at 1.6 ppm (^2J = 8.0 Hz) for the green complexes (**4b**). The methylene of –N–CH$_2$–(Ph) of green **4c** appears as a singlet at 5.5 ppm. The difference in the stereochemical description of the two chelating azoimine groups in the blue-violet isomer, **5**, has been ascribed from the inequivalent AB type splitting of –CH$_2$– in –N–CH$_2$–(CH$_3$) (**5b**) and –N–CH$_2$–(Ph) (**5c**). There are, however, neither neighbouring chiral centers nor any appreciable bond rotational barrier but a distorted coordination around the metal centre does exist. This overall distortion may lead to molecular dissymmetry [14,20].

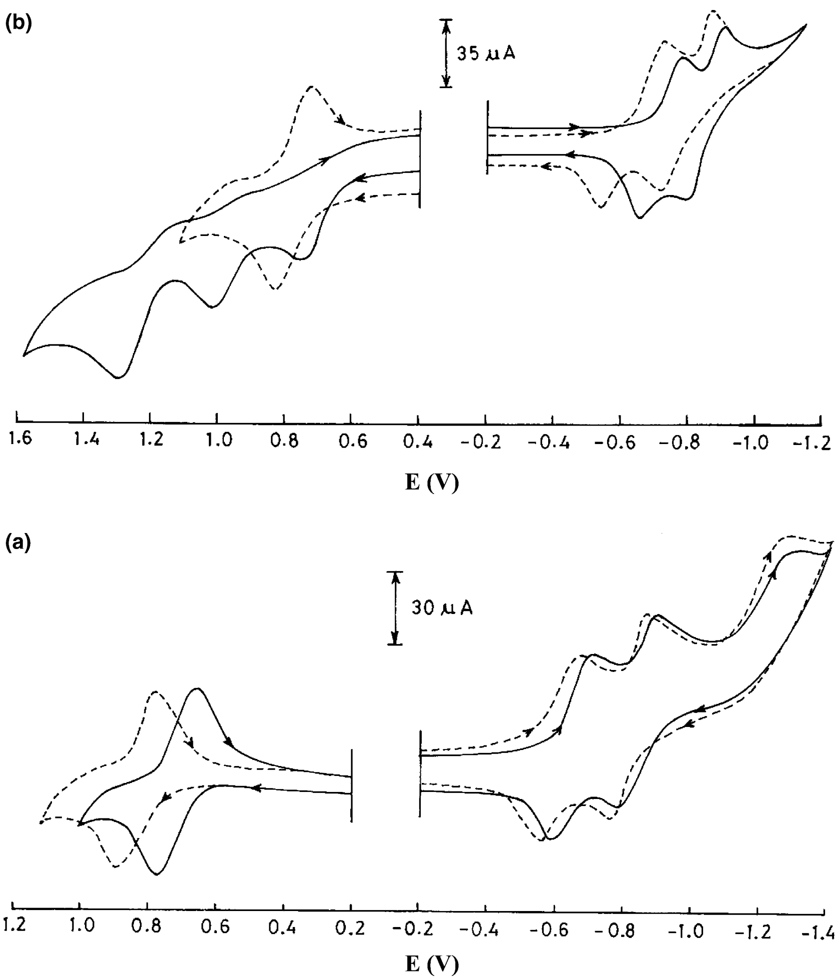

Fig. 2. Cyclic voltammogram of (a) **4b** (—), **5b** (- - -); (b) **6b** (—), **7b** (- - -).

Table 2
^{1}H NMR data[a] recorded of ruthenium complexes (**4**–**7**) at 298 K

Compounds	δ, ppm (*J*, Hz)							
	4-H[b]	5-H[b]	7-H[c]	9-H[b]	10-H[d]	11-H[b]	N(1)–R	PPh_3-protons[e]
(**4b**)	7.20 (7.0)	7.07 (7.0)	8.65	7.84 (9.0)	7.50 (9.0)	8.33 (9.0)	4.10[f]	
(**4c**)	7.21 (7.0)	7.06 (7.0)	8.61	7.82 (8.5)	7.51 (9.0)	8.35 (8.5)	4.44 (12.0),[g] 1.58 (8.0)[d]	
(**4d**)	7.18 (7.0)	7.00 (7.0)	8.60	7.78 (9.0)	7.46 (9.0)	8.35 (9.0)	5.35[h]	
(**5b**)	7.22 (7.0)	7.05 (7.0)	8.62	7.80 (9.0)	7.45 (9.0)	8.32 (9.0)	4.14[f]	
(**5c**)	7.25 (7.0)	7.10 (7.0)	8.68	7.85 (8.5)	7.53 (9.0)	8.41 (8.5)	4.35 (12.0),[g] 1.48 (8.0)[d]	
(**5d**)	7.22 (7.0)	7.06 (7.0)	8.65	7.82 (9.0)	7.48 (9.0)	8.39 (9.0)	5.54, 5.27 (22.0)[g]	
(**6a**)	7.15 (6.0)	7.02 (6.0)	8.51	7.62 (9.0)	7.42 (9.0)	8.36 (6.0)	5.97[i]	7.30–7.50
(**6b**)	7.16 (6.0)	7.05 (6.0)	8.55	7.65 (9.0)	7.46 (9.0)	8.35 (6.0)	4.22[f]	7.30–7.45
(**6c**)	7.18 (6.0)	7.08 (6.0)	8.57	7.66 (9.0)	7.47 (9.0)	8.34 (6.0)	4.50 (12.0),[g] 1.48 (8.0)[d]	7.30–7.45
(**6d**)	7.29 (7.0)	7.09 (7.0)	8.56	7.69 (9.0)	7.49 (9.0)	8.33 (6.0)	6.00[h]	7.25–7.50
(**7a**)	7.22 (7.0)	7.08 (7.0)	8.55	7.70 (9.0)	7.50 (9.0)	8.41 (7.0)	5.80[i]	7.30–7.50
(**7b**)	7.18 (7.0)	7.05 (7.0)	8.58	7.72 (9.0)	7.48 (9.0)	8.42 (7.0)	4.20[f]	7.30–7.45
(**7c**)	7.16 (7.0)	7.05 (7.0)	8.56	7.70 (9.0)	7.47 (9.0)	8.43 (7.0)	4.45 (12.0),[g] 1.60 (8.0)[d]	7.30–7.45
(**7d**)	7.22 (7.0)	7.07 (7.0)	8.61	7.75 (9.0)	7.54 (9.0)	8.45 (7.0)	5.85[h]	7.25–7.50

[a] In $CDCl_3$.
[b] Doublet.
[c] Singlet.
[d] Triplet.
[e] Multiplet.
[f] 1-CH_3.
[g] Quartet for –CH_2–.
[h] 1-CH_2(Ph), and δ(Ph): 7.4–7.5 ppm.
[i] N(1)–H, broad.

Imidazole 4-H and 5-H appear as doublet signals at 7.1–7.2 and 7.0–7.1 ppm, respectively. A singlet signal appearing at the most downfield position, 8.6 ppm, is unambiguously assigned to 7-H. The second highest chemical shift is observed at 8.3 ppm which is a doublet signal ($^2J = 9.0$ Hz) and is assigned to 11-H. Two other protons 9-H and 10-H appear as a doublet and triplet at ca. 7.8 and 7.5 ppm, respectively.

Redox activities of the complexes have been examined by cyclic voltammetry. Fig. 2 shows four redox responses in the potential range 1.2 to −1.4 V versus SCE (Table 1) in MeCN. A couple positive to SCE at 0.7–0.8 V is oxidative in nature. This is quasireversible in nature as evident from ΔE_p values (>90 mV). This is referred to the Ru(III)/Ru(II) couple. Three reduction responses appear negative to SCE and are quasireversible in nature. The chelated azoimine (–N=N–C=N–) groups are well known π-acidic agents which have low lying azo-centered π^*-molecular orbitals. Thus, the reductions are referred to electron accommodation at LUMOs characterized by the azo function.

The potential data (Table 1) related to the blue-violet isomers (**5**) exhibit higher redox potentials by 0.1–0.2 V than those of the green isomers (**4**). An increase in stability of the Ru(II) state in the blue-violet isomer (**5**) may be due to a cisoid orientation of the azoimine function. In *ctc*-Ru(3′-PyaiR)$_2$Cl$_2$ (**5**) the back bonding interaction may in turn occur with two different dπ-orbitals, while in the *trans*-orientation two groups will compete for the same dπ-orbitals. This may be associated with the increase in effective charge on the ruthenium in **5** and may shift the Ru(III)/Ru(II) couple to more positive values than in **4**. The present set of Ru(III)/Ru(II) redox potential data are higher than Ru(RaaiR′)$_2$Cl$_2$ (RaaiR′ = 1-alkyl-2-(arylazo)imidazole) [14] but lower than Ru(aapm)$_2$Cl$_2$ (aapm = 2-(arylazo)pyrimidine) [19]. This suggests that the π-acidity order of the ligands is as follows: arylazoimidazole < pyridylazoimidazole < arylazopyrimidine.

2.2. Ruthenium carbonyl complexes of 3′-PyaiR

2.2.1. Synthesis and formulation

Ru(CO)$_3$(PPh$_3$)$_2$ has been used as a starting material in the synthesis of mixed ligand Ru(0)-carbonyl compounds. In extremely moisture free conditions under a dinitrogen atmosphere, Ru(CO)$_3$(PPh$_3$)$_2$ has been reacted with 3′-PyaiR in MeCN under reflux for 2–2.5 h.

$$\mathrm{Ru(CO)_3(PPh_3)_2} + 3'\text{-PyaiR} \rightarrow \underset{\mathbf{6}}{\mathrm{Ru(CO)_3}(3'\text{-PyaiR})\mathrm{(PPh_3)_2}} + 2\mathrm{CO} \qquad (2)$$

3′-PyaiR is an efficient π-acidic chelating agent and acts as an effective CO supplement in the stabilization of low metal oxidation states. The product isolated after filtration has been purified by a chromatography process. The complexes are extremely stable and remain unchanged upon exposure to air even in solution for a month. The composition of the complexes, Ru(CO)(3′-PyaiR)(PPh$_3$)$_2$ (**6**) has been supported by microanalytical data. The complexes are non-electrolytes and are diamagnetic.

2.2.2. X-ray structure determination

The X-ray structure of Ru(CO)(3′-PyaiH)(PPh$_3$)$_2$ (**6a**) has been determined and is shown in Fig. 3. Selected bond parameters are listed in Table 3. The molecule consists of a central Ru atom surrounded by five coordination centers and the arrangement is quite a regular square pyramid. The atomic arrangement involves two *trans*-phosphines, cheated pyridylazo-imidazole and a CO within the RuP$_2$N$_2$C coordination sphere. The atomic group Ru, N(1), C(1), N(4), N(3) constitute a chelate plane (rms deviation ⩽0.031 Å). The 3′-pyridyl ring is inclined at an angle of 37.38(15)° with the chelate ring. The *trans*-phosphine angle, P(1)–Ru–P(2) is 167.62 (2)° and lies in the lower

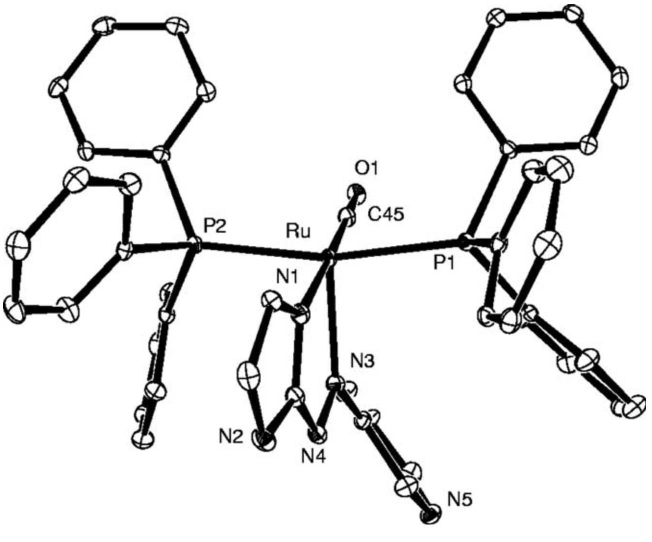

Fig. 3. X-ray structure of Ru(3′-PyaiH)(CO)(PPh$_3$)$_2$ (**6a**).

Table 3
Selected bond distances (Å) and angles (°) for [Ru(CO)(3′-PyaiH)(PPh$_3$)$_2$] (**6a**) along with their esd in parentheses

Distances (Å)		Angles (°)	
Ru–C(45)	1.8545(13)	N(1)–Ru–N(3)	73.79(8)
Ru–N(1)	2.111(2)	N(1)–Ru–C(45)	176.04(7)
Ru–N(3)	2.1938(19)	N(3)–Ru–C(45)	103.79(7)
Ru–P(1)	2.3605(7)	N(1)–Ru–N(3)	73.79(8)
Ru–P(2)	2.3478(7)	Ru–N(1)–C(1)	112.97(16)
N(3)–N(4)	1.284(3)	Ru–N(3)–N(4)	117.93(15)
N(1)–C(1)	1.347(3)	P(1)–Ru–P(2)	167.62(2)
		P(1)–Ru–C(45)	88.54(4)
		P(2)–Ru–C(45)	89.10(4)
		P(1)–Ru–N(1)	94.79(6)
		P(1)–Ru–N(3)	95.40(5)
		P(2)–Ru–N(1)	88.10(6)
		P(2)–Ru–N(3)	96.96(5)

range of reported data [27–34]. This large deviation from *trans*-angle values may be due to steric crowding. The chelate bite angle N(1)–Ru–N(3) is 73.79(8)°. Other angles around Ru define a distorted quite regular pyramidal geometry.

The Ru–N(3) (N(3) is the azo–N) bond length of 2.194(2) Å is slightly longer than Ru–N(1) (N(1) is imidazole) (2.112(3) Å). This is unusual to the structural chemistry of Ru–azoheterocycles [14–18]. The N=N distance is 1.284(3) Å and is longer than the free ligand value (1.268(2) Å) [32]. It is elongated due to dπ(Ru) $\rightarrow$ π^*(azo) charge transfer. The observed Ru–P distances are very short (2.3478(7), 2.3605(7) Å) in the series of Ru(PPh$_3$) chemistry [30–33]. Ru(0) may be associated with PPh$_3$ by strong π-back bonding which causes shortening of the Ru–P distances. Ru(0) is a better donor than Ru(II) and this may support the shortening of the Ru–P distances.

The Ru–C bond length (1.8545(13) Å) is comparable with the data reported for the Ru(II)-carbonyl system [27,33,34]. This shows that the Ru(0) oxidation state has little influence on the Ru–CO distance. The C–O bond length is 1.141(4) Å and is also insignificantly influenced by the zero oxidation state of ruthenium. The EHMO results also support this data (Fig. 4).

2.2.3. Spectra and bonding

The complexes [Ru(CO)(3′-PyaiR)(PPh$_3$)$_2$] (**6**) show a sharp stretch at ca. 1925 cm^{-1} that corresponds to ν(CO). Presence of a single ν(CO) band is in support of a ‘Ru(CO)’ type carbonyl derivative [33,34]. Other significant stretchings are ν(N=N) and ν(C=N) at 1410–1415 and 1580–1600 cm^{-1}, respectively. Comparisons of the infrared data for monocarbonyl ruthenium/osmium complexes of other heterocyclic–N chelators [27,33,34] also helped us to identify the present series of complexes.

The complexes are sparingly soluble in non-polar solvents but reasonably soluble in polar solvents. The electronic spectra of the complexes in MeCN show a high intense transition at 360–380 nm (inter-ligand charge transfer) with a reasonably intense shoulder at 460–470 nm (Table 1, Fig. 1). The absorption at 460–470 nm may be assigned to a transition involving metal orbitals, e.g., d–d, MLCT/LMCT type. Upon excitation at 365 nm the complexes give an observable emission at the longer wavelength of 418–426 nm in MeCN, which originates from the (π–π^*) type.

To explain the electronic properties of the complexes, extended Huckel calculation were performed using crystallographic parameters of [Ru(CO)(3′-PyaiH)(PPh$_3$)$_2$]. Some

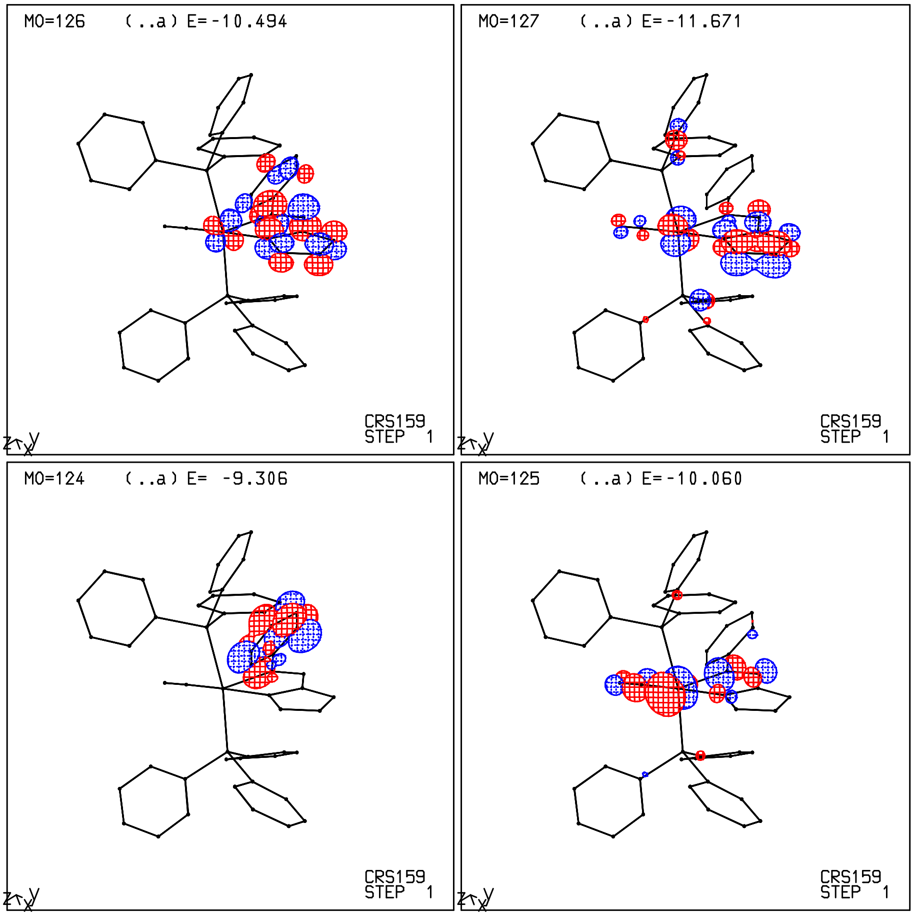

Fig. 4. EHMO plots of HOMO − 1, HOMO, LUMO, LUMO + 1 MO = 127 (HOMO − 1) Ru 46%, 3′-PyaiH = 33%, azo = 10%; MO = 126 (HOMO) Ru = 16%, 3′-PyaiH = 78%, azo = 48%; MO = 125 (LUMO) Ru = 63%, 3′-PyaiH = 19%, azo = 17%, CO = 10%; MO = 124 (LUMO + 1) Ru = 0%, 3′-PyaiH = 99%.

of the MOs are shown in Fig. 4. The transition HOMO → LUMO may be assigned to a LMCT transition; since the HOMO is composed of 78% ligand function and the LUMO brings 63% metal function. Thus the electronic transition at 460–470 nm may be assigned to a LMCT and the intense band at 370–380 comprises intra-ligand transitions. Emission spectra observed upon excitation at 365 nm thus originate from a ligand centered π–π^* state.

The ^{1}H NMR spectra of the complexes (**6**) were carried out in $CDCl_3$. Data are set out in Table 2. Imidazole protons, 4- and 5-H, appear as a pair of doublets at 7.2–7.4 and 7.0–7.1 ppm, respectively. A singlet appears at 8.5 ppm and is assigned to 7-H. Other signals are also assigned on comparing with the free ligand data [26]. The 1-R signals appear in their usual positions. 1-Me appears as a singlet at 4.2 ppm; 1-CH_2-CH_3 gives a quartet (4.5 ppm, ($J = 12.0$ Hz)) and a triplet (1.5 ppm ($J = 8.0$ Hz)); 1-CH_2-(Ph) gives a singlet at 6.00 ppm. PPh_3 shows multiplets at 7.3–7.5 ppm. Because of the low solubility in $CDCl_3$ we could not perform ^{13}C NMR spectral measurements.

2.2.4. Electrochemistry

The redox data are summarised in Table 1 and a representative voltammogram is shown in Fig. 2. An initial scan (+ve to SCE) from 0.0 to 1.8 V shows three responses at 0.6–0.7, 0.9–1.0 and 1.2–1.3 V. Scan reversal does not give cathodic peak potentials and suggests irreversibility of the electrochemical reaction. The nature of the redox program does not change with scan rate (50–250 mV S^{-1}). Ru(0) in the complexes **6** can sequentially exhibit Ru(I)/Ru(0), Ru(II)/Ru(I) and Ru(III)/Ru(II) redox processes. We do not have any definite proof to the existence of these redox couples. Because of small difference in E_{pa} (peak potential) values we could not perform coulometric oxidation at a definite potential, and oxidation at the highest potential (>1.4 V) does not complete the coulomb count. This may be due to participation of the solvent in oxidation. The solution colour changes to bright brown red. We did not proceed further.

On scanning to the negative direction (0 to −1.8 V) three redox responses are observed. First two responses are quasireversible ($\Delta E_p \geqslant 100$ mV) and the third one appears at <−1.2 V which is irreversible in nature. The chelated ligand belongs to a π-acidic family and can accommodate two electrons centered at the azo group (–N=N–). On comparing with literature information [14–20], we may assign the first two reductive responses (−0.7 and −0.9 V) as azo reductions [–N=N–]/[–NN$\cdots$N]$^{-}$ and [–NN$\cdots$N]$^{-}$/[–N–N–]$^{2-}$.

2.2.5. Reaction with Cl_2

$$\mathrm{Ru(CO)(3'\text{-}PyaiR)(PPh_3)_2 + Cl_2} \xrightarrow[\mathrm{NaClO_4(aq)}]{\mathrm{MeCN}} \underset{\mathbf{7}}{\mathrm{[Ru(CO)Cl(3'\text{-}PyaiR)(PPh_3)_2](ClO_4)}} \qquad (3)$$

A MeCN solution of the complex was stirred with a Cl_2 saturated solution in the same solvent for 15 min. The solution colour changed from brown to red-brown within a few minutes. The solution was evaporated to dryness, washed with cold water and extracted with chloroform. The solution was chromatographed and eluted by MeCN–MeOH (3:2, v/v). To a methanolic solution of the brown mass $NaClO_4$(aq) was added and a dark coloured precipitate was filtered and then washed with cold water.

The dry mass was chromatographed over silica gel, prepared in benzene. An orange brown band was eluted by MeCN and evaporated slowly in air. Crystalline compound **7** (40–50%) was then separated. A black mass was adhered on the column head and rejected. The molar conductance data in MeCN solutions ($\Lambda_M = 70$–$90\ \Omega^{-1}\ M^{-1}\ cm^{-1}$) suggested a 1:1 electrolyte. The complex may exist in two different isomeric forms. However, we could not separate them by the chromatographic process. So the spectral property may be referred to the mixture of isomeric data. Infrared spectra of the complexes show a strong sharp stretch at 1085–1090 cm^{-1} along with a weak transmission at 625–630 cm^{-1}. This corresponds to $\nu(ClO_4)$. A sharp strong stretch at 1953–1965 cm^{-1} is assigned to ν(CO), which is blue shifted by 30–35 cm^{-1} compared to ν(CO) of the precursor, [Ru(CO)$(PPh_3)_2$(3′-PyaiR)]. This is obviously due to weakening of the π-back donation ability of Ru(II) in the product compared to Ru(0). Additionally, a weak stretch is observed at 310–320 cm^{-1} which is absent in precursor. This is assigned to a ν(Ru–Cl) stretch. Other significant stretchings are ν(N=N) at 1410–1400 and ν(C=N) at 1590–1600 cm^{-1}. We could not crystallize this complex to get a good single crystal for X-ray analysis.

The solution electronic spectra of these complexes exhibit absorptions at 500–510, 400–390 and 350–280 nm (Table 1, Fig. 1). The longer wavelength band, which is absent in the precursor, is assigned to a dπ(Ru) → π^* (3′-PyaiR), MLCT transition. Other transitions may be ligand centered (LC) transitions. The cyclic voltammogram of [Ru(CO)Cl(3′-PyaiR)$(PPh_3)_2$](ClO_4) (**5**) shows a quasireversible oxidative response at >0.7 V. This refers to the Ru(III)/Ru(II) redox process (Fig. 2). Ligand centered reductions are observed at <−0.6 V and correspond to electron addition to the –N=N– bond.

3. Conclusion

Pyridylazoimidazole (3′-PyaiR) stabilizes the Ru(0) state in collaboration with CO and PPh_3. The structure shows quite a regular square pyramid of the formula Ru(CO)$(PPh_3)_2$(3′-PyaiR) (**6**). Cl_2 oxidation has isolated the Ru(II) complex [Ru(CO)Cl(3′-PyaiR)$(PPh_3)_2$](ClO_4) (**7**). Upon oxidation ν(CO) is blue shifted by 30–35 cm^{-1}. The electronic and ^{1}H NMR spectra are also reported. Cyclic voltammograms shows irreversible oxidations corresponding to Ru(0) → Ru(I), Ru(I) → Ru(II) and Ru(II) → Ru(III) while **6** shows a quasireversible Ru(II) → Ru(III) oxidation. Ligand reductions are usually observed at the azo centre. Ru(II) complexes of the formula Ru(3′-PyaiR)$_2Cl_2$ are isolated from the reaction between $RuCl_3$ and 3′-PyaiR.

Two isomers, green tcc-Ru(3′-PyaiR)$_2$Cl$_2$ and blue-violet ctc-Ru(3′-PyaiR)$_2$Cl$_2$ are also characterised.

4. Experimental

4.1. Materials and methods

3-Aminopyridine was purchased from Lancaster, UK. Imidazole and all other organic chemicals and inorganic salts were available from the Sisco Research Lab, Mumbai, India. Ru(CO)$_3$(PPh$_3$)$_2$ was synthesized as in the reported procedure [33]. For the solution spectral studies, spectroscopic grade solvents were used from Lancaster, UK. Microanalyses (C, H, N) were performed using a Perkin–Elmer 2400 CHNO elemental analyzer. Spectroscopic measurements were carried out using the following instruments: UV–Vis spectra, JASCO UV–Vis/NIR model V-570; IR spectra (KBr disk, 4000–200 cm^{-1}), JASCO FT-IR model 420; ^{1}H NMR spectra in CDCl$_3$ and CD$_3$CN Bruker 300 MHz FT-NMR spectrometers in the presence of TMS as internal standard. Molar conductances (Λ_M) were measured in a Systronics conductivity meter 304 model using ca. 10^{-3} M solutions in DMSO. Silver is measured gravimetrically. Emission was examined by a F-4500 Hitachi spectrofluorimeter at room temperature (298 K) in MeCN under non-degassed conditions.

4.1.1. Synthesis of the ligands 3′-(pyridyazo)imidazole

Pyridylazoimidazole is a new class of unsymmetric biheterocycle and has been synthesized by coupling the diazonium salt of 3-aminopyridine with imidazole in Na$_2$CO$_3$ solution. N(1)-alkylation has been performed by the reported method using RX in dry THF in the presence of NaH. The chromatographic process has been used to purify the N(1)-alkylated product. Detailed procedures have been reported earlier [26].

*4.1.2. Preparation and separation of tcc- and ctc-[Ru(3′-PyaiMe)$_2$Cl$_2$] (**4** and **5**)*

A degassed dry ethanol (10 ml) solution of 3-PyaiMe (0.25 g, 1.34 mmol) was added slowly using a pressure equalising funnel to a green Ru(II) solution (prepared by reduction of RuCl$_3 \cdot 3$H$_2$O (0.17 g, 65 mmol) in 10 ml dry ethanol and refluxed for 3 h under nitrogen environment). The volume of the solution was reduced to half of its original volume by nitrogen bubbling and was kept in refrigerator overnight. The precipitate so obtained was filtered and washed with water, cold ethanol and finally with ether. It was then dried over CaCl$_2$. A CH$_2$Cl$_2$ solution of the dry mass was chromatographed over silica gel prepared in petroleum ether (60–80 °C). A green band was eluted by toluene–acetonitrile (9:1 v/v) and a blue violet band was collected using toluene–acetonitrile (3:2 v/v). The solutions were evaporated in air and crystalline products were isolated in 35% and 20% yields.

The microanalytical data of the complexes are as follows: *Anal.* Calc. for C$_{18}$H$_{18}$N$_{10}$Cl$_2$Ru (**4b**): C, 39.47; H, 3.39; N, 25.71. Found: C, 39.56; H, 3.30; N, 25.64%. *Anal.* Calc. for C$_{22}$H$_{22}$N$_{10}$Cl$_2$Ru (**4c**): C, 41.74; H, 3.88; N, 24.30. Found: C, 41.81; H, 3.83; N, 24.39%. *Anal.* Calc. for C$_{30}$H$_{26}$N$_{10}$Cl$_2$Ru (**4d**): C, 51.65; H, 3.66; N, 20.00. Found: C, 51.58; H, 3.72; N, 20.06%. *Anal.* Calc. for C$_{18}$H$_{18}$N$_{10}$Cl$_2$Ru (**5b**): C, 39.50; H, 3.25; N, 25.70. Found: C, 39.56; H, 3.30; N, 25.64%. *Anal.* Calc. for C$_{22}$H$_{22}$N$_{10}$Cl$_2$Ru (**5c**): C, 41.78; H, 3.78; N, 24.30. Found: C, 41.81; H, 3.83; N, 24.39%. *Anal.* Calc. for C$_{30}$H$_{26}$N$_{10}$Cl$_2$Ru (**5d**): C, 51.65; H, 3.66; N, 20.00. Found: C, 51.58; H, 3.72; N, 20.06%.

*4.1.3. Preparation of [Ru(CO)(PPh$_3$)$_2$(3′-PyaiH)] (**6a**)*

To a solution of [Ru(CO)$_3$(PPh$_3$)$_2$] (0.200 g, 0.282 mmol) in MeCN (20 ml) was added 3′–PyaiH (0.05 g, 0.289 mmol) in acetonitrile. The solution was stirred for 8 h. The yellow solution turned red. The solution was filtered and evaporated slowly. Red coloured crystals developed after four days. The crystals were collected by filtration, washed with cold water–acetonitrile (1:1, v/v) and dried over CaCl$_2$ in vacuo. The yield was 0.16 g (78%). The microanalytical data of the complexes are as follows: *Anal.* Calc. for C$_{45}$H$_{37}$N$_5$OP$_2$Ru (**6a**): C, 65.37; H, 4.48; N, 8.47. Found: C, 65.29; H, 4.43; N, 8.39%. *Anal.* Calc. for C$_{46}$H$_{39}$ C$_{46}$H$_{39}$N$_5$OP$_2$Ru (**6b**): C, 65.71; H, 4.64; N, 8.33. Found: C, 65.66; H, 4.60; N, 8.27%. *Anal.* Calc. for C$_{47}$H$_{41}$N$_5$OP$_2$Ru (**6c**): C, 66.04; H, 4.80; N, 8.20. Found: C, 65.96; H, 4.76; N, 8.15%. *Anal.* Calc. for C$_{52}$H$_{43}$ N$_5$OP$_2$Ru (**6d**): C, 68.12; H, 4.69; N,7.64. Found: C, 68.06; H, 4.65; N, 7.58%.

*4.1.4. Oxidation of [Ru(CO)(PPh$_3$)$_2$(3′-PyaiMe)] by Cl$_2$ (**6b**)*

To a MeCN solution (15 ml) of [Ru(CO)(PPh$_3$)$_2$(3′-PyaiMe)] (0.2 g, 0.24 mmol) 3 ml of Cl$_2$ saturated MeCN solution was added, dropwise, and stirred. The solution colour changed immediately from brown red to orange red. The solution was stirred for 30 min and then evaporated in air to reduce its volume to half of its original value. Upon addition of a 2 ml saturated solution of NaClO$_4$ to this solution, a dark coloured compound precipitated. This was then filtered, washed with water and dried over CaCl$_2$. The CH$_2$Cl$_2$ solution of the dry mass was chromatographed over silica gel prepared in petroleum ether (60–80 °C). A deep orange red band was eluted by MeCN–toluene (1:3, v/v) and a black mass was attached on the column head. The solution was evaporated via rotary evaporation and the solid product was recrystallised by diffusion of a CH$_2$Cl$_2$ solution to hexane. Yield, 0.14 g, 60%.

The other compounds were prepared by an identical procedure and the yield varied from 60% to 65%.

The microanalytical data of the complexes are as follows: *Anal.* Calc. for C$_{45}$H$_{37}$N$_5$O$_5$P$_2$Cl$_2$Ru (**7a**): C, 56.26; H, 3.80; N, 7.17. Found: C, 56.19; H, 3.85; N, 7.28%. *Anal.*

Table 4
Summarised crystallography data for [Ru(CO)(3′-pyaiH)(PPh_3)$_2$] (**6a**)

Crystal parameters	
Empirical formula	$C_{45}H_{37}N_5OP_2Ru$
Formula weight	826.81
Crystal system	monoclinic
Space group	*Cc*
a (Å)	12.2952 (8)
b (Å)	19.3393 (8)
c (Å)	16.7572 (8)
β (°)	104.0670 (10)
Size	$0.25 \times 0.20 \times 0.10$
V (Å^3)	3865.0 (4)
λ (Å)	0.71073
ρ_{calc} (Mg m^{-3})	1.421
Z	4
T (K)	295 (2)
μ(Mo Kα) (mm^{-1})	0.531
2θ	$4.02 \leqslant 2\theta \leqslant 56.7$
hkl	$-15 \leqslant h \leqslant 16$, $-25 \leqslant k \leqslant 24$, $-22 \leqslant l \leqslant 22$
Reflection collected	20133
Observed data ($I > 2\sigma(I)$)	7363
Refined parameters	481
R	0.0293
wR_2	0.0462
Goodness-of-fit[a]	0.832

$w = 1/[\sigma^2(F_o^2) + (0.0214P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

[a] Goodness-of-fit is defined as $[w(F_o^2 - F_c^2)/(n_0 - n_v)]^{1/2}$ where n_0 and n_v denote the number of data and variables, respectively.

Calc. for $C_{46}H_{39}N_5O_5P_2Cl_2Ru$ (**7b**): C, 56.57; H, 4.08; N, 7.07. Found: C, 56.73; H, 4.00; N, 7.19%. *Anal.* Calc. for $C_{47}H_{41}N_5O_5P_2Cl_2Ru$ (**7c**): C, 57.07; H, 4.08; N, 7.23. Found: C, 57.14; H, 4.15; N, 7.09%. *Anal.* Calc. for $C_{52}H_{43}N_5O_5P_2Cl_2Ru$ (**7d**): C, 59.40; H, 4.17; N, 6.75. Found: C, 59.49; H, 4.10; N, 6.67%.

4.2. X-ray diffraction study

Crystals of [Ru(CO)(3′-PyaiH)(PPh_3)$_2$] (**6a**) were grown by slow diffusion of a CH_2Cl_2 solution of the complex into hexane. Crystal parameters and refinement results are summarized in Table 4. Data were collected on a Bruker SMART CCD diffractometer using graphite monochromatised Mo Kα radiation ($\lambda = 0.71073$ Å) at 295(2) K. Data collections were performed in the 2θ range 4–56°. Empirical absorption corrections were carried out based on ψ and ω-scans. The structure was solved by direct methods and refined by full-matrix least-squares refinement based on F_o^2 and including all reflections. All non-hydrogen atoms were refined anisotropically. Data reduction, structure solution and refinement were performed with SHELX-97.

5. Supporting information available

Crystallographic data for structural analysis are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033 (e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk) on request, quoting the CCDC No. 256887.

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