Study of novel η^5-cyclopentadienyl and η^6-arene platinum group metal complexes containing a N_4-type ligand and their structural characterization

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ABSTRACT

The mononuclear η^5-cyclopentadienyl complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$, $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$ and pentamethylcyclopentadienyl complex $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ react in the presence of 1 eq. of the tetradentate N,N'-chelating ligand 3,5-bis(2-pyridyl)pyrazole (bpp-H) and 1 eq. of NH_4PF_6 in methanol to afford the mononuclear complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(bpp\text{-}H)]PF_6$ ($[\mathbf{1}]PF_6$), $[(\eta^5\text{-}C_5H_5)Os(PPh_3)(bpp\text{-}H)]PF_6$ ($[\mathbf{2}]PF_6$) and $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(bpp\text{-}H)]PF_6$ ($[\mathbf{3}]PF_6$), respectively. The dinuclear η^5-pentamethylcyclopentadienyl complexes $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}Cl)Cl]_2$ and $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}Cl)Cl]_2$ as well as the dinuclear η^6-arene ruthenium complexes $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl]_2$ and $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(\mu\text{-}Cl)Cl]_2$ react with 2 eq. of bpp-H in the presence of NH_4PF_6 or NH_4BF_4 to afford the corresponding mononuclear complexes $[(\eta^5\text{-}C_5Me_5)Rh(bpp\text{-}H)Cl]PF_6$ ($[\mathbf{4}]PF_6$), $[(\eta^5\text{-}C_5Me_5)Ir(bpp\text{-}H)Cl]PF_6$ ($[\mathbf{5}]PF_6$), $[(\eta^6\text{-}C_6H_6)Ru(bpp\text{-}H)Cl]BF_4$ ($[\mathbf{6}]BF_4$) and $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(bpp\text{-}H)Cl]BF_4$ ($[\mathbf{7}]BF_4$). However, in the presence of 1 eq. of bpp-H and NH_4BF_4 the reaction with the same η^6-arene ruthenium complexes affords the dinuclear salts $[(\eta^6\text{-}C_6H_6)_2Ru_2(bpp)Cl_2]BF_4$ ($[\mathbf{8}]BF_4$) and $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)_2Ru_2(bpp)Cl_2]BF_4$ ($[\mathbf{9}]BF_4$), respectively. These compounds have been characterized by IR, NMR and mass spectrometry, as well as by elemental analysis. The molecular structures of $[\mathbf{1}]PF_6$, $[\mathbf{5}]PF_6$ and $[\mathbf{8}]BF_4$ have been established by single crystal X-ray diffraction studies and some representative complexes have been studied by UV–vis spectroscopy.

1. Introduction

Within the large family of η^5- and η^6-cyclichydrocarbon metal complexes, piano–stool complexes of ruthenium are undeniably the most studied class of complexes. They have found applications in catalysis, supramolecular assemblies and molecular devices, and have shown antiviral, antibiotic and anticancer activities. These three-legged piano–stool complexes possess a pseudo-octahedral geometry at the metal center, the arene ligand occupying three coordinating sites (the seat) with three other ligands (the legs). Therefore, the octahedral geometry can be viewed as pseudo-tetrahedral, thus limiting the number of possible isomers.

Transition metal complexes containing polypyridyl ligands are associated with interesting photochemical and electrochemical properties [1–8], and they are used as catalysts [9,10], multi-electron storage systems [11–13], in the design of new materials [14–17] and as molecular devices [18–22]. Complexes with these ligands are also potential DNA intercalators with an ability to inhibit nucleic acid synthesis [23]. Recently, metal polypyridyl complexes have been widely used as building blocks [24–27]. The

occurrence of isomers by the synthetic assembly of mononuclear building blocks is a major problem in the design of supramolecular systems.

Half-sandwich complexes have proved to be extremely useful in stoichiometric and catalytic asymmetric syntheses, and therefore, have attracted lot of attention [28–31]. In addition, the four coordinated, pseudo-tetrahedral geometry makes them particularly suitable for investigation of the stereochemistry of reactions at the metal center [32]. Many studies of cyclopentadienyl and arene ruthenium(II) complexes with bidentate ligands have shown that substitution reactions occur predominantly with retention of the configuration at the metal center [33]. A few studies have been carried out on pentamethylcyclopentadienyl rhodium(III) and iridium(III) complexes with polypyridyl ligands [34]. The reactivity of ruthenium(II), osmium(II), rhodium(III) and iridium(III) with various polypyridyl ligands has been reported [35–37].

In this paper, we report a series of η^5-cyclopentadienyl ruthenium, osmium, η^5-pentamethylcyclopentadienyl ruthenium, rhodium and iridium and η^6-arene ruthenium complexes with a tetradentate N,N'-donor ligand, *viz.* 3,5-bis(2-pyridyl)pyrazole (bpp-H) (see below). The 3,5-bis(2-pyridyl)pyrazole (bpp-H) ruthenium metal complexes are associated with being an extremely interesting water oxidation catalyst [38,39]. This ligand can act as

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a bidentate as well as tetradentate ligand depending on the ratio of metal-to-ligand used. The molecular structures of representative compounds are reported as well.
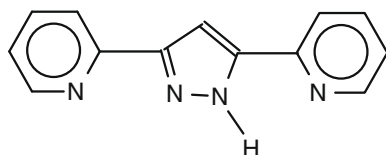
Ligand used in this study

2. Experimental

2.1. Physical measurements

Elemental analyses were performed on a Perkin–Elmer-2400 CHN/O analyzer. Infrared spectra were recorded on a Perkin–Elmer Model 983 spectrophotometer with the sample prepared as KBr pellets. The ^{1}H NMR spectra were recorded on a Bruker ACF-400 (400 MHz) spectrometer in CDCl$_3$ solvent with TMS as the internal reference. All chemicals used were of reagent grade. All reactions were carried out in distilled and dried solvents. Ruthenium trichloride trihydrate, iridium trichloride, rhodium trichloride and osmium tetraoxide (OsO$_4$) were purchased from Arora Matthey Ltd. The 3,5-bis(2-pyridyl)pyrazole (bpp-H) was prepared by following a literature procedure [40,41]. The precursor complexes [(η^5-C$_5$H$_5$)Ru(PPh$_3$)$_2$Cl] [33,42,43], [(η^5-C$_5$H$_5$)Os(PPh$_3$)$_2$Br] [44,45], [(η^5-C$_5$Me$_5$)Ir(μ-Cl)Cl]$_2$, [(η^5-C$_5$Me$_5$)Rh(μ-Cl)Cl]$_2$ [46], [(η^5-C$_5$Me$_5$)Ru(PPh$_3$)$_2$Cl] [47], [(η^6-C$_6$H$_6$)Ru(μ-Cl)Cl]$_2$ and [(η^6-p-^{i}PrC$_6$H$_4$Me)Ru(μ-Cl)Cl]$_2$ [48–50], were prepared by following the reported literature methods.

2.2. Single-crystal X-ray structure analyses

Crystals suitable for X-ray diffraction studies for compounds [**1**]PF$_6$ and [**5**]PF$_6$ were grown by slow diffusion of wet diethylether

into a dichloromethane solution of [**1**]PF$_6$, and [**5**]PF$_6$, respectively. Whereas in the case of compound [**8**]BF$_4$, crystals were grown by slow diffusion of wet diethylether into an acetonitrile solution of [**8**]BF$_4$. A bright red crystal of [**1**]PF$_6$ · H$_2$O and a pale green crystal of [**5**]PF$_6$ were mounted on a Stoe-Image Plate Diffraction System equipped with a ϕ circle goniometer, using Mo Kα graphite monochromated radiation ($\lambda = 0.71073$ Å) with the ϕ range 0–200°, increment of 1.2°, $D_{max} - D_{min} = 12.45$–0.81 Å. Whereas a crystal of [**8**]BF$_4$ · H$_2$O was mounted on a Bruker Apex CCD diffractometer in the full reciprocal sphere equipped with a CCD detector, X-ray intensity data were collected with Mo Kα graphite monochromated radiation at 120 (2) K, with a 0.3°ω scan mode and 10 s per frame. The intensity data were corrected for Lorenz and polarization effects. The structures were solved by direct methods using the program SHELXS-97 [51]. Refinement and all further calculations were carried out using SHELXL-97 [52]. The H-atoms were included in calculated positions and were treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. The data collection parameters and bond lengths and angles are presented in Tables 1 and 2, respectively.

2.3. Preparation of [(η^5-C$_5$H$_5$)M(bpp-H)(PPh$_3$)]PF$_6$ {M = Ru [**1**]PF$_6$, Os [**2**]PF$_6$}

A mixture of [(η^5-C$_5$H$_5$)M(PPh$_3$)$_2$X] {M = Ru, X = Cl and M = Os, X = Br} (100 mg, 0.11 mmol), 3,5-bis(2-pyridyl)pyrazole (bpp-H) (50 mg, 0.22 mmol) and NH$_4$PF$_6$ (36 mg, 0.22 mmol) in dry methanol (15 ml) were refluxed under dry nitrogen for 8 h until the color of the solution changed from pale yellow to orange. The solvent was removed under vacuum, the residue was dissolved in dichloromethane (10 ml) and the solution was filtered to remove ammonium halide. The orange solution was concentrated to 5 ml, and upon addition of diethylether the orange–yellow complex precipitated, which was separated and dried under vacuum.

Complex [(η^5-C$_5$H$_5$)Ru(bpp-H)(PPh$_3$)]PF$_6$ [**1**]PF$_6$: Yield: 75 mg, 68.4%. Elemental *Anal*. Calc. for C$_{36}$H$_{30}$N$_4$P$_2$F$_6$Ru: C, 54.3; H, 3.7; N, 7.1. Found: C, 54.87; H, 4.13; N, 7.94%. IR (KBr pellets, cm^{-1}): 3429 (ν_{N-H}); 1460 ($\nu_{C=N}$); 850 (ν_{P-F}). ^{1}H NMR (CDCl$_3$, δ): 9.31 (d,

Table 1
Crystallographic and structure refinement parameters for complexes [**1**]PF$_6$ · H$_2$O, [**5**]PF$_6$ and [**8**]BF$_4$ · H$_2$O.

	[**1**]PF$_6$	[**5**]PF$_6$ · H$_2$O	[**8**]BF$_4$ · H$_2$O
Chemical formula	C$_{36}$H$_{30}$F$_6$N$_4$P$_2$Ru	C$_{23}$H$_{27}$ClF$_6$IrN$_4$OP	C$_{25}$H$_{23}$BCl$_2$F$_4$N$_4$ORu$_2$
Formula weight	795.65	748.11	755.32
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	Pc (no. 7)	$P2_1/c$ (no. 14)
Crystal color and shape	green block	red block	orange plate
Crystal size	0.32 × 0.20 × 0.20	0.25 × 0.24 × 0.21	0.22 × 0.13 × 0.04
a (Å)	13.663(1)	8.760(1)	14.229(7)
b (Å)	14.426(1)	13.903(2)	11.265(6)
c (Å)	17.172(1)	13.706(2)	16.008(8)
β (°)	104.284(8)	129.18(1)	95.750(5)
V (Å^3)	3280.1(4)	1293.8(3)	2553(2)
Z	4	2	4
T (K)	173(2)	173(2)	120(2)
D_{calc} (g cm^{-3})	1.611	1.920	1.965
μ (mm^{-1})	0.644	5.393	1.451
Scan range (°)	2.09 < θ < 26.00	2.41 < θ < 26.02	2.21 < θ < 28.21
Unique reflections	6310	4670	5885
Reflections used [$I > 2\sigma(I)$]	5334	3109	5452
R_{int}	0.0542	0.1067	0.0230
Flack parameter		−0.06(3)	
Final R indices [$I > 2\sigma(I)$]*	0.0324, wR_2 0.0854	0.0715, wR_2 0.1780	0.0252, wR_2 0.0622
R indices (all data)	0.0414, wR_2 0.0940	0.0942, wR_2 0.1872	0.0282, wR_2 0.0647
Goodness-of-fit	1.008	0.932	1.026
Max., min. $\Delta\rho$/e (Å^{-3})	0.662, −1.640	4.068, −4.524	0.758, −0.415

* Structures were refined on F_0^2: $wR_2 = [\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma w(F_0^2)^2]^{1/2}$, where $w^{-1} = [\Sigma(F_0^2) + (aP)^2 + bP]$ and $P = [\max(F_0^2, 0) + 2F_c^2]/3$.

Table 2
Selected bond lengths and angles for complexes [**1**]PF$_6$, [**5**]PF$_6$ · H$_2$O and [**8**]BF$_4$ · H$_2$O.

Distances (Å)	[**1**]PF$_6$	[**5**]PF$_6$ · H$_2$O	[**8**]BF$_4$ · H$_2$O
N(1)–M(1)	2.188(2)	2.07(8)	2.103(2)
N(2)–M(1)	2.085(2)	2.01(5)	2.096(2)
Cl(1)–M(1)		2.398(17)	2.403(13)
N(2)–N(3)	1.342(3)	1.37(8)	1.350(3)
M(1)–CNT(1)	1.830	1.786	1.685
N(3)–M(2)			2.090(2)
N(4)–M(2)			2.090(2)
Cl(2)–M(2)			2.4339(14)
M(2)–CNT(2)			1.681
Angles (°)			
N(3)–N(2)–M(1)	135.60(15)	135(4)	135.49(14)
N(2)–M(1)–N(1)	75.75(8)	77(2)	76.63(8)
N(2)–M(1)–Cl(1)		83.1(15)	87.4
N(1)–M(1)–Cl(1)		87.9(15)	87.1
N(2)–N(3)–M(2)			136.49(15)
N(3)–M(2)–N(4)			76.83(8)
N(4)–M(2)–Cl(2)			82.77(6)
N(3)–Ru(2)–Cl(2)			87.43(5)

1H); 8.55 (d, 1H); 8.06 (s, 1H); 7.8 (td, 1H); 7.75 (d, 2H); 7.62 (m, 2H); 7.45 (m, 2H); 4.75 (s, 5H, C$_5$H$_5$); 7.32–7.2 (m, 15H, PPh$_3$). ^{31}P {^{1}H} NMR (CDCl$_3$, δ): 50.83 (s, PPh$_3$). ESI-MS (m/z): 651.1 [M–PF$_6$], 650.1 [M–PF$_6$–H], 389.0 [M–PF$_6$–PPh$_3$]. UV–vis [(CH$_3$CN; λ_{max}, nm (ε, M^{-1} cm^{-1})]: 329 (24000).

Complex [(η^5-C$_5$H$_5$)Os(bpp-H)(PPh$_3$)]PF$_6$ [**2**]PF$_6$: Yield: 65 mg, 66.7%. Elemental *Anal.* Calc. for C$_{36}$H$_{30}$N$_4$P$_2$F$_6$Os: C, 48.9; H, 3.4; N, 6.3. Found: C, 49.2; H, 3.91; N, 6.87%. IR (KBr pellets, cm^{-1}): 3425 (ν_{N-H}); 1474 ($\nu_{C=N}$); 850 (ν_{P-F}). ^{1}H NMR (CDCl$_3$, δ): 9.2 (d, 1H); 8.55 (d, 1H); 8.45 (s, 1H); 7.81 (td, 1H); 7.78 (d, 1H); 7.7 (m, 2H); 7.38 (m, 1H); 6.9 (t, 2H); 4.69 (s, 5H, C$_5$H$_5$); 7.3–7.25 (m, 15H, PPh$_3$). ESI-MS (m/z): 740.3 [M–PF$_6$], 739.2 [M–PF$_6$–H], 478.3 [M–PF$_6$–PPh$_3$].

2.4. Preparation of [(η^5-C$_5$Me$_5$)Ru(bpp-H)(PPh$_3$)]PF$_6$ [**3**]PF$_6$

A mixture of [(η^5-C$_5$Me$_5$)Ru(PPh$_3$)$_2$Cl] (100 mg, 0.125 mmol), 3,5-bis(2-pyridyl)pyrazole (bpp-H) (56 mg, 0.25 mmol) and NH$_4$PF$_6$ (40 mg, 0.25 mmol) in dry methanol (15 ml) were refluxed under dry nitrogen for 12 h until the color of the solution changed from pale yellow to orange. The solvent were removed in a rotary evaporator under reduced pressure, the residue was dissolved in dichloromethane (10 ml), and the solution filtered to remove ammonium chloride. The orange solution was concentrated to 5 ml, when addition of excess hexane gave the orange–yellow complex, which was separated and dried under vacuum. Yield: 70 mg, 64.3%. Elemental *Anal.* Calc. for C$_{41}$H$_{45}$N$_4$P$_2$F$_6$Ru: C, 56.6; H, 5.2; N, 6.4. Found: C, 57.0; H, 5.9; N, 6.8%. IR (KBr pellets, cm^{-1}): 3424(ν_{N-H}); 1613 ($\nu_{C=N}$); 850 (ν_{P-F}). ^{1}H NMR (CDCl$_3$, δ): 11.92 (s,1H); 8.7 (d, 1H); 8.5 (s, 1H); 7.8 (td, 1H); 7.6 (d, 1H); 7.28 (t, 2H); 7.1 (m, 1H); 6.89 (t, 2H); 1.45 (s, 15H); 7.33–7.18 (m, 15H, PPh$_3$). ^{31}P {^{1}H} NMR (CDCl$_3$, δ): 49.72 (s, PPh$_3$). ESI-MS (m/z): 722.3 [M–PF$_6$], 460.3 [M–PF$_6$–PPh$_3$]. UV–vis [(CH$_3$CN; λ_{max}, nm (ε, M^{-1} cm^{-1})]: 358 (17000).

2.5. Preparation of [(η^5-C$_5$Me$_5$)M(bpp-H)Cl]PF$_6$ {M = Rh [**4**]PF$_6$, Ir [**5**]PF$_6$}

A mixture of [(η^5-C$_5$Me$_5$)M(μ-Cl)Cl]$_2$ (M = Rh, Ir) (Rh dimer = 100 mg, 0.16 mmol and Ir dimer = 125 mg, 0.16 mmol), 3,5-bis(2-pyridyl)pyrazole (bpp-H) (70 mg, 0.325 mmol) and NH$_4$PF$_6$ (50 mg, 0.325 mmol) in dry methanol (15 ml) were stirred at room temperature for 6 h until the color of the solution changed from pale yellow to pale green. The solvents were removed in a rotary evaporator under reduced pressure, the residue was dissolved in dichloromethane (5 ml), and the solution filtered to remove ammonium chloride. The pale green solution was concentrated to 2 ml, when addition of excess hexane gave the orange–yellow complex, which was separated and dried under vacuum.

Complex [**4**]PF$_6$: Yield: 70 mg, 76%. Elemental *Anal.* Calc. for C$_{23}$H$_{25}$N$_4$PClF$_6$Rh: C, 37.8; H, 3.4; N, 7.7. Found: C, 38.0; H, 3.9; N, 7.0%. IR (KBr pellets, cm^{-1}): 3426 (ν_{N-H}); 1612 ($\nu_{C=N}$); 850 (ν_{P-F}). ^{1}H NMR (CDCl$_3$, δ): 11.80 (s, 1H); 8.9 (d, 1H); 8.6 (d, 1H); 8.2 (td, 1H); 8.0 (s,1H); 7.5 (t, 2H); 7.4 (t, 1H); 7.2 (t, 2H); 1.48 (s, 15H). ESI-MS (m/z): 494.2 [M–PF$_6$], 459.2 [M–PF$_6$–Cl]. UV–vis [(CH$_3$CN; λ_{max}, nm (ε, M^{-1} cm^{-1})]: 308 (26000).

Complex [**5**]PF$_6$: Yield: 68 mg, 74.1%. Elemental *Anal.* Calc. for C$_{23}$H$_{25}$N$_4$ClPF$_6$Ir: C, 43.1; H, 3.9; N, 8.7. Found: C, 43.6; H, 4.2; N, 8.0%. IR (KBr pellets, cm^{-1}): 3429 (ν_{N-H}); 1613 ($\nu_{C=N}$); 850 (ν_{P-F}). ^{1}H NMR (CDCl$_3$, δ): 11.86 (s,1H); 8.75 (d,1H); 8.58 (d, 1H); 8.45 (td, 1H); 8.24 (s, 1H); 7.5 (t, 2H); 7.4 (t, 2H); 7.2 (t, 1H); 1.45 (s, 15H). ESI-MS (m/z): 583.2 [M–PF$_6$], 548.2 [M–PF$_6$–Cl].

2.6. Preparation of [(η^6-C$_6$H$_6$)Ru(bpp-H)Cl]BF$_4$ [**6**]BF$_4$

A mixture of [(η^6-C$_6$H$_6$)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.1 mmol), 3,5-bis(2-pyridyl)pyrazole (bpp-H) (88 mg, 0.395 mmol) and NH$_4$BF$_4$ (52 mg, 0.496 mmol) was stirred in dry methanol (15 ml) for 4 h at room temperature. The solvent was rotary evaporated. The solid was dissolved in dichloromethane and then filtered to remove ammonium chloride. The solution was concentrated to 2 ml and excess of diethylether was added for precipitation. The light brown color product was separated out, washed with ether and dried in vacuum. Yield: 70 mg, 67.3%. Elemental *Anal.* Calc. for C$_{19}$H$_{16}$N$_4$BClF$_4$Ru: C, 42.75; H, 4.91; N, 10.50. Found: C, 42.6; H, 5.0; N, 10.41%. IR (KBr pellets, cm^{-1}): 3416 (ν_{N-H}); 1613 ($\nu_{C=N}$); 1082 (ν_{B-F}). ^{1}H NMR (CDCl$_3$, δ): 9.2 (d, 1H), 8.79 (d, 1H), 8.65 (s, 1H), 7.98 (t, 2H), 7.84 (d, 2H), 7.45 (m, 2H), 7.38 (m, 1H), 6.25 (s, 6H). ESI-MS (m/z): 437 [M–BF$_4$], 435.9 [M–BF$_4$–H]. UV–vis [(CH$_3$CN; λ_{max}, nm (ε, M^{-1} cm^{-1})]: 318 (14000).

2.7. Preparation of [(η^6-p-^{i}PrC$_6$H$_4$Me)Ru(bpp-H)Cl]BF$_4$ [**7**]BF$_4$

A mixture of [(η^6-C$_{10}$H$_{14}$)Ru(μ-Cl)Cl]$_2$ (100 mg, 0.163 mmol), 3,5-bis(2-pyridyl) pyrazole (bpp-H) (144 mg, 0.65 mmol) and NH$_4$BF$_4$ (85 mg, 0.81 mmol) was stirred in dry methanol (15 ml) for 4 h at room temperature. The yellow compound which formed was filtered, washed with ethanol and diethylether, and dried under vacuum. Yield: 140 mg, 74%. Elemental *Anal.* Calc. for C$_{23}$H$_{24}$N$_4$BClF$_4$Ru: C, 47.65; H, 4.17; N, 9.66. Found: C, 47.5; H, 4.1; N, 9.61%. IR (KBr pellets, cm^{-1}): 3416 (ν_{N-H}); 1613 ($\nu_{C=N}$); 1082 (ν_{B-F}). ^{1}H NMR (CDCl$_3$, δ): 9.2 (d, 1H), 8.64 (d, 1H), 8.53 (d, 1H), 7.95 (t, 2H), 7.84 (d, 2H), 7.8 (m, 2H), 7.36 (t, 1H), 6.51 (d, 1H, Ar$_{p-cy}$), 6.1 (d, 1H, Ar$_{p-cy}$), 5.88 (d, 1H, Ar$_{p-cy}$), 5.78 (d, 1H, Ar$_{p-cy}$), 2.63 (sep, 1H), 2.32 (s, 3H), 1.03 (d, 6H). ESI-MS (m/z): 492.1 [M–BF$_4$], 491.1 [M–BF$_4$–H], 457.1[M–BF$_4$–Cl]. UV–vis [(CH$_3$CN; λ_{max}, nm (ε, M^{-1} cm^{-1})]: 430 (10000).

2.8. Preparation of [(η^6-C$_6$H$_6$)$_2$Ru$_2$(bpp)Cl$_2$]BF$_4$ [**8**]BF$_4$

A mixture of [(η^6-C$_6$H$_6$)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.10 mmol), 3,5-bis(2-pyridyl)pyrazole (bpp-H) (22 mg, 0.10 mmol) and NH$_4$BF$_4$ (51 mg, 0.49 mmol) was stirred in dry methanol (15 ml) for 4 h at room temperature. The brown compound which formed was filtered, washed with methanol and diethylether, and dried under vacuum. Yield: 50 mg, 67.9%. Elemental *Anal.* Calc. for C$_{25}$H$_{23}$N$_4$BCl$_2$F$_4$ORu$_2$: C, 39.75; H, 3.07; N, 7.42. Found: C, 39.6; H, 3.0; N, 7.38%. IR (KBr pellets, cm^{-1}): 3416 (ν_{N-H}); 1613 ($\nu_{C=N}$); 1082 (ν_{B-F}). ^{1}H NMR (CDCl$_3$, δ): 8.91 (d, 1H), 8.5 (d, 1H), 8.35 (t, 2H), 8.12 (s, 1H), 7.92 (m, 2H), 7.7 (d, 1H), 7.55 (d, 1H), 6.35 (s, 6H), 6.1 (s, 6H). ESI-MS (m/z): 650.9 [M–BF$_4$], 649.9 [M–BF$_4$–H].

UV–vis [(CH$_3$CN; λ_{max}, nm (ε, M^{-1} cm^{-1})]: 328 (18 000), 424 (3000).

2.9. Preparation of [(η^6-p-^{i}PrC$_6$H$_4$Me)$_2$Ru$_2$(bpp)Cl$_2$]BF$_4$ [9]BF$_4$

A mixture of [(η^6-C$_{10}$H$_{14}$)Ru(μ-Cl)Cl]$_2$ (100 mg, 0.163 mmol), 3,5-bis(2-pyridyl)pyrazole (bpp-H) (36 mg, 0.16 mmol) and NH$_4$BF$_4$ (85 mg, 0.81 mmol) was stirred in dry methanol (15 ml) for 4 h at room temperature. The pale yellow compound which formed was filtered, washed with methanol and diethylether, and dried under vacuum. Yield: 95 mg, 68.44%. Elemental *Anal*. Calc. for C$_{33}$H$_{37}$N$_4$BCl$_2$F$_4$Ru$_2$: C, 46.66; H, 4.39; N, 6.60. Found: C, 46.5; H, 4.4; N, 6.7%. IR (KBr pellets, cm^{-1}): 3416 (ν_{N-H}); 1613 ($\nu_{C=N}$); 1082 (ν_{B-F}). ^{1}H NMR (CDCl$_3$, δ): 9.1 (s,1H); 8.8 (d, 1H); 8.77 (d, 1H); 8.37 (t, 1H); 7.95 (t, 2H); 7.93 (s, 1H); 7.68 (t, 1H); 6.46 (d, 1H); 6.09 (d, 1H, Ar$_{p-cy}$), 6.01 (d, 1H, Ar$_{p-cy}$), 5.99 (d, 2H, Ar$_{p-cy}$); 2.67 (sep, 1H), 2.17 (s, 3H), 1.04 (d,6H). ESI-MS (m/z): 763 [M−BF$_4$], 762.0 [M−BF$_4$−H]. UV–vis [(CH$_3$CN; λ_{max}, nm (ε, M^{-1} cm^{-1})]: 322 (19 000), 425 (3000).

3. Results and discussion

The mononuclear η^5-cyclic hydrocarbon complexes [(η^5-C$_5$H$_5$)Ru(PPh$_3$)$_2$Cl], [(η^5-C$_5$H$_5$)Os(PPh$_3$)$_2$Br] and [(η^5-C$_5$Me$_5$)-Ru(PPh$_3$)$_2$Cl] react with 3,5-bis(2pyridyl)pyrazole (bpp-H) in the presence of ammonium hexafluorophosphate in methanol to form the mononuclear cationic cyclopentadienyl ruthenium and cyclopentadienyl osmium complexes having the general formula [(η^5-C$_5$H$_5$)M(bpp-H)PPh$_3$]$^+$ (M = Ru [1]PF$_6$; M = Os [2]PF$_6$) and pentamethylcyclopentadienyl ruthenium complex having the formula [(η^5-C$_5$Me$_5$)Ru(bpp-H)PPh$_3$]$^+$ ([3]PF$_6$) (Chart 1). The complexes are orange–yellow, non-hygroscopic, air stable, crystalline solids. They are soluble in polar solvents such as methanol, dichloromethane, chloroform and acetone, but insoluble in hexane, petroleum ether and diethylether.

3.1. Cyclopentadienyl ruthenium [1]PF$_6$ and osmium [2]PF$_6$ complexes

The analytical data of these compounds are consistent with the formulations (Chart 1). These complexes are formed by the reaction of metal complexes with the bpp-H ligand, irrespective of the metal-to-ligand ratio, yielding only mononuclear compounds. Attempts to make dinuclear complexes by increasing the metal complex ratio were unsuccessful, which might be due to the steric bulkiness of the complex due to the presence of the triphenylphosphine group. The infrared spectra of the complexes [1]PF$_6$ and [2]PF$_6$ exhibit a chelated *N,N'*-bidentate ligand with strong bands at 3429, 3425, 1460 and 1474 cm^{-1} corresponding to the stretching frequencies of the N–H bond of the pyrazole ring and the C–N bond of the pyridine ring of the ligand. In addition, the infrared spectra contained a strong band at 850 cm^{-1} due to the stretching frequency of the P–F bond of PF$_6$ for both the complexes. The proton NMR spectra of these complexes exhibit a singlet at 4.75 and 4.69 ppm for the cyclopentadienyl ring protons, indicating a

downfield shift from the starting complexes [(η^5-C$_5$H$_5$)Ru(PPh$_3$)$_2$Cl] and [(η^5-C$_5$H$_5$)Os(PPh$_3$)$_2$Br] [42,45]. The downfield shift in the position of the cyclopentadienyl protons might result from a change in the electron density on the metal center due to chelation of the 3,5-bis(2-pyridyl)pyrazole (bpp-H) ligand through two nitrogen atoms. In addition to the other ligand peaks, as mentioned in the Section 2, a multiplet in the range 7.3–7.2 ppm, which corresponds to the phenyl protons of the triphenylphosphine group of these complexes, is observed.

The 3,5-bis(2-pyridyl)pyrazole (bpp-H) ligand reacts with the pentamethylcyclopentadienyl ruthenium(II) complexes in the presence of NH$_4$PF$_6$ in methanol, to yield the mononuclear cationic complex [(η^5-C$_5$Me$_5$)Ru(PPh$_3$)(bpp-H)]PF$_6$ ([3]PF$_6$) (Chart 1). The complex is an orange crystalline solid, soluble in polar solvents and air stable. The infrared spectrum displays a sharp band at 3424, 1613 and 850 cm^{-1}, corresponding to the stretching frequencies of the N–H bond of the pyrazole ring, the C–N bond of the pyridine ring and the P–F bond of the counter ion of the complex. In addition to the proton peaks of the ligand, as mentioned in the Section 2, the proton NMR spectrum also displays a singlet peak at 1.45 ppm corresponding to the methyl protons of the pentamethylcyclopentadienyl ring and a multiplet in the range 7.3–7.2 ppm which corresponds to the phenyl protons of the triphenylphosphine group. The ^{31}P {^{1}H} NMR spectra of the complexes [1]PF$_6$ and [3]PF$_6$ exhibit a single sharp resonance for triphenylphosphine at 50.8 and 49.7 ppm, respectively, whereas for the starting complexes [(η^5-C$_5$H$_5$)Ru(PPh$_3$)$_2$Cl] and [(η^5-C$_5$Me$_5$)Ru(PPh$_3$)$_2$Cl] the signals appear at 42.0 and 38.5 ppm, respectively [33,42, 43,47]. The structure of a representative complex, [1]PF$_6$, was solved by a single crystal X-ray diffraction study (Fig. 1).

3.2. Pentamethylcyclopentadienyl rhodium [4]PF$_6$ and iridium complexes [5]PF$_6$

The dinuclear complexes [(η^5-C$_5$Me$_5$)M(μ-Cl)Cl]$_2$ (M = Rh or Ir) undergo a bridge cleavage reaction with the *N,N'*-bidentate nitrogen base (bpp-H) ligand in methanol at room temperature, leading to the formation of the chloride displaced complexes [4]PF$_6$ and [5]PF$_6$, respectively (Scheme 1).

These complexes were isolated as their hexafluorophosphate salts. Here also we were only able to isolate the mononuclear complexes, despite the lack of triphenylphosphine groups. Change in concentration and longer reaction times do not change the reaction pathways. The orange–yellow complexes are air stable, soluble in polar solvents but insoluble in hexane, petroleum ether and diethylether. Complex [4]PF$_6$ exhibits a pale green color when dissolved in solution. The infrared spectra of the complexes [4]PF$_6$ and [5]PF$_6$ exhibit for the chelated *N,N'*-bidentate ligand, strong bands at 3426, 1612, 3429 and 1613 cm^{-1}, corresponding to the stretching frequencies of the C–N bond of the pyridine group and the N–H bond of the pyrazole ring. In addition, the infrared spectra contain a strong band at 850 cm^{-1} due to the ν_{P-F} stretching frequency of PF$_6$. The proton NMR spectra of compounds [4]PF$_6$ and [5]PF$_6$ displays a singlet at 1.48 and 1.45 ppm, corresponding to the protons
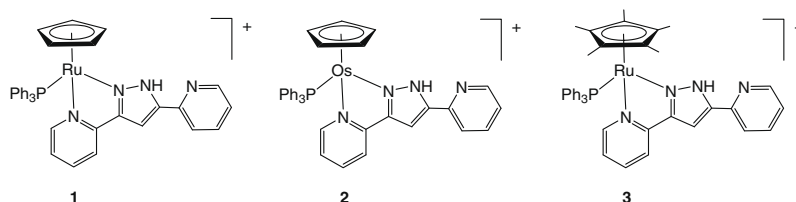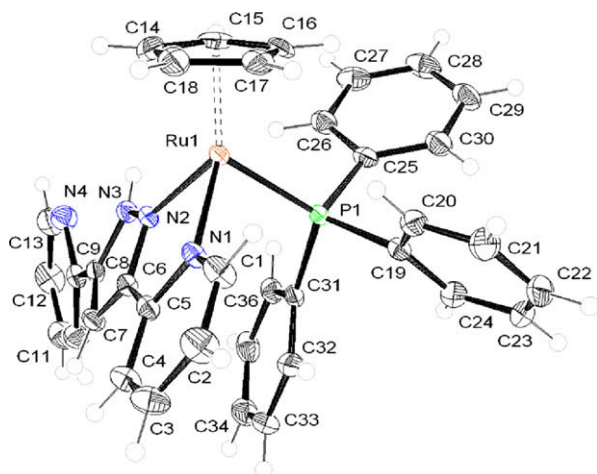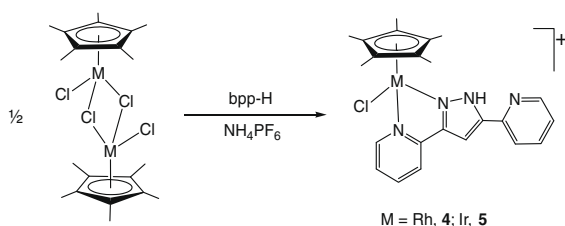

Chart 1.

Fig. 1. ORTEP diagram with the labeling scheme for [(Cp)Ru(bpp-H)(PPh₃)]⁺ ([**1**]PF₆), at the 50% probability level, the PF₆ anion is omitted for clarity.

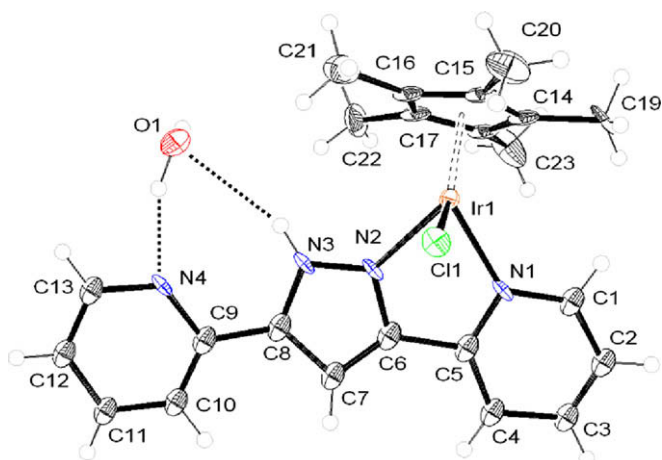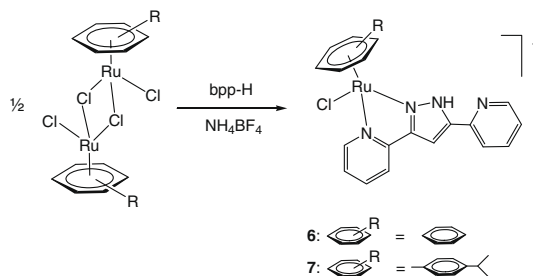**Scheme 1.**

of the pentamethylcyclopentadienyl group. The molecular structure of the complex [**5**]PF₆ was solved by single crystal X-ray crystallography and the structure is presented in Fig. 2.

3.3. Mononuclear arene ruthenium complexes [6]BF₄ and [7]BF₄ and dinuclear complexes [8]BF₄ and [9]BF₄

The dinuclear arene ruthenium complexes [(η⁶-arene)RuCl₂]₂ (arene = benzene and *p*-cymene) react with the *N,N*′-based ligand (bpp-H) in methanol to produce the mononuclear cationic complexes [**6**]BF₄ and [**7**]BF₄ (Scheme 2) and the dinuclear cationic complexes [**8**]BF₄ and [**9**]BF₄ (Scheme 3). The complexes [**6**]BF₄

Fig. 2. ORTEP diagram with the labeling scheme for [(η⁵-C₅Me₅)Ir(bpp-H)Cl]⁺ ([**5**]PF₆ · H₂O), at the 50% probability level, the PF₆ anion is omitted for clarity.
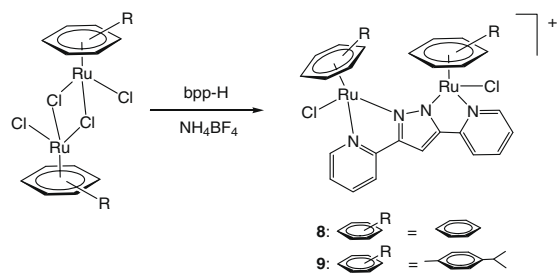

Scheme 2.

and [**7**]BF₄ are brown in color in solution, while they are yellow, non-hygroscopic, air stable solids. The complexes [**8**]BF₄ and [**9**]BF₄ are also yellow, non-hygroscopic, air stable solids, but they are sparingly soluble in polar solvents like dichloromethane, chloroform, acetone and acetonitrile, and are insoluble in non-polar solvents like hexane, diethylether and petroleum ether.

These complexes display strong bands at 3416 and 1613 cm⁻¹ corresponding to the stretching frequencies of the N–H bond of the pyrazole ring and the C–N bond of the pyridine ring. In addition, the IR spectra of all these complexes contain a strong band at 1082 cm⁻¹ due to the stretching frequency of the B–F bond of the counter ion of these complexes. In complex [**6**]BF₄, in addition to the proton peaks of the ligand, the NMR spectra also displays a singlet at around 6.25 ppm which corresponds to the six protons of the benzene ring. Whereas in the case of the dinuclear complex [**8**]BF₄, in addition to the ligand peaks, the spectra displays two singlet in the range of 6.3–6.1 ppm which corresponds to the protons of the two benzene rings. The formation of these compounds is also confirmed by ESI-MS spectrometry. The presence of peaks at *m/z* = 651.1, 740.3, 722.3, 658.5, 748.2, 437.2, 650.9, 492.1 and 763, which coincides with the molecular mass of the cationic complexes [**1**]PF₆ to [**9**]BF₄, also confirms the formation of these compounds.

An interesting point to make here is when the starting dimers [(η⁶-arene)RuCl₂]₂ (arene = benzene, *p*-cymene and hexamethylbenzene) are treated with terpyridine in methanol, rapid displacement of the arene group with terpyridine takes place to form a ruthenium terpyridine complex. In contrast, when [**8**]BF₄ or [**9**]BF₄ is treated with terpyridine, the reaction does not occur, i.e., the direct displacement of the arene group by terpyridine is not possible [53,54]. This could be due to the following reasons: (i) The formation of a mononuclear complex, as a solvated cationic complex in the case of [(η⁶-arene)RuCl₂]₂, is not possible in the case of [**8**]BF₄ or [**9**]BF₄. (ii) In these complexes the arene binds to the metal with *fac*-coordination, it is difficult then to replace this with *mer*-coordinating ligands such as terpyridine due to the frozen free rotation of ligands, unlike in the starting dimers. These complexes are prepared by different methods [38,39]. The dinuclear structure of representative complex [**8**]BF₄ was further confirmed by its molecular structure determination from a single crystal X-ray study (Fig. 3).

4. UV–vis spectroscopy

The UV–vis spectra of the representative complexes [**1**]PF₆, [**3**]PF₆, [**4**]PF₆, [**6**]BF₄, [**7**]BF₄, [**8**]BF₄ and [**9**]BF₄ were acquired in acetonitrile, and spectral data are summarized in the Section 2. Mononuclear complexes [**1**]PF₆, [**3**]PF₆, [**4**]PF₆ and [**6**]BF₄ displayed an intense transition in the UV region. The high energy absorption bands in the electronic spectra of [**1**]PF₆, [**3**]PF₆, [**4**]PF₆ and [**6**]BF₄ in the UV region at ∼308–358 nm and have been assigned to ligand-centered π → π*/n → π* transitions [55], whereas in the case of [**7**]BF₄, it shows a low energy absorption band in the visible

Scheme 3.

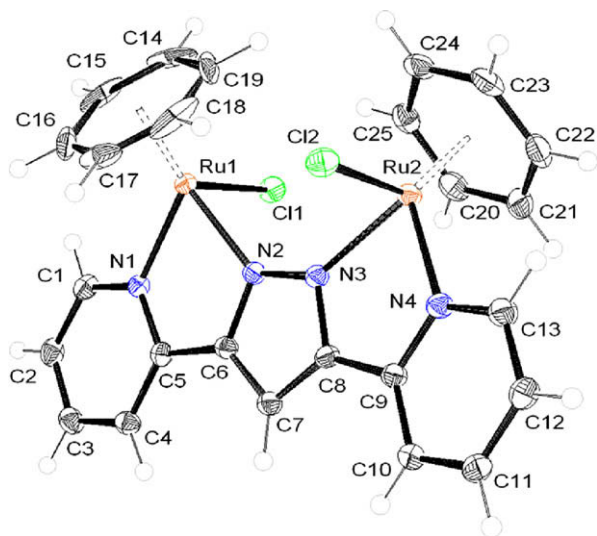**Fig. 3.** ORTEP diagram with the labeling scheme for [(η⁶-C₆H₆)₂Ru₂(bpp)Cl₂]⁺ ([**8**]BF₄ · H₂O), at the 50% probability level, the water and BF₄ anion are omitted for clarity.

region at ~430 nm which can be assigned to a MLCT transition. The dinuclear complexes [**8**]BF₄ and [**9**]BF₄ exhibited similar trends, with an additional band at ~425 nm that can be assigned to the MLCT band due to a $d\pi$M-arene $\to \pi^*_{bpp}$ transition [55], and they exhibit significant red shifts. In general, these complexes follow the normal trends observed in the electronic spectra of nitrogen bonded metal complexes, which display ligand based $\pi \to \pi^*/n \to \pi^*$ transitions in the UV region and metal-to-ligand charge transfer transitions in the visible region. The electronic spectra of these complexes are shown in Fig. 4.

5. Molecular structures

The molecular structures of [(η⁵-C₅H₅)Ru(bpp-H)PPh₃]PF₆ ([**1**]PF₆) [(η⁵-C₅Me₅)Ir(bpp-H)Cl]PF₆ · H₂O ([**5**]PF₆) and [(η⁶-C₆H₆)₂Ru₂(bpp)Cl₂]BF₄·H₂O ([**8**]BF₄) have been established by single-crystal X-ray analysis of their hexafluorophosphate and tetrafluoroborate salts. The complexes show a typical piano–stool geometry with the metal center coordinated by the cyclopentadienyl or arene ligand, a terminal chloride in complexes [**5**]PF₆ and [**8**]BF₄, triphenylphosphine in complex [**1**]PF₆ and the chelating bpp-H ligand. The metal atom is in an octahedral arrangement with two *cis*-nitrogen atoms of the bpp-H ligand acting as a bidentate chelating ligand through the neighboring pyridyl and pyrazolyl nitrogen atoms. In this study, the mononuclear complexes [**1**]PF₆ and [**5**]PF₆ were found to be coordinated to N1 and N2, and the dinuclear complex [**8**]BF₄ was found to have the first metal center coordinated to N1 and N2 and the second metal center coordinated

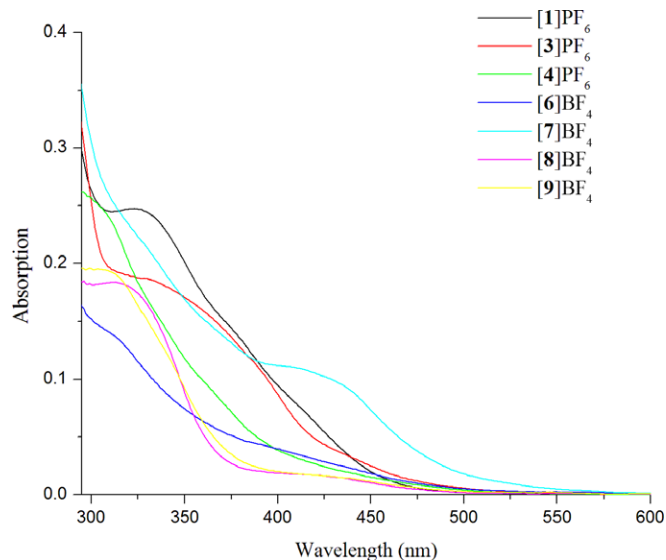**Fig. 4.** UV–Visible spectra of the complexes [**1**]PF₆, [**3**]PF₆, [**4**]PF₆, [**6**]BF₄, [**7**]BF₄, [**8**]BF₄ and [**9**]BF₄ in acetonitrile at 298 K.

to N3 and N4 in a five-membered ring chelating fashion involving nitrogen atoms of the pyridine and the pyrazolyl moiety, respectively. The aromatic ring occupies three coordinate sites in these complexes to complete the octahedral geometry around the metal center. The molecular structures of complexes [**1**]PF₆, [**5**]PF₆ and [**8**]BF₄ are shown in Figs. 1–3, respectively. Selected bond lengths and angles are presented in Table 2.

The distances between the iridium atom and the centroid of the η⁵-C₅Me₅ ring is 1.786 Å in complex [**5**]PF₆, whereas the distance betwen the ruthenium atom and the centroid of the η⁵-C₅H₅ ring is 1.830 Å in complex [**1**]PF₆. These bond distances are comparable to those in the related complex cations [(η⁵-C₅Me₅)IrCl(C₅H₄ N-2-CH=N–C₆H₄–p–X)]⁺, where X = NO₂ and Cl [56] and [Ru(η⁵-C₅H₅)(PPh₃)(κ²-paa)]⁺ and [Ru(η⁵-C₅H₅)(κ¹-dppm)(κ²-paa)]⁺ [57]. Whereas in the complex [**8**]BF₄, the distances between the metal and the centeriod of the arene rings are 1.685 and 1.681 Å, which are in accordance with the values reported in other related complexes [58].

All these complexes crystallize in monoclinic space groups. The complexes [**5**]PF₆ and [**8**]BF₄ crystallize with a molecule of water per asymmetric unit. The M–N distance in complex [**5**]PF₆ appears to be significantly shorter than the M–N distances in complexes [**1**]PF₆ and [**8**]BF₄. There are no significant differences in the C–C bond lengths in the pentamethylcyclopentadienyl ring, all being about 1.337 Å and pointing to uniform π-electron delocalization in the ring. Furthermore, the five-membered ring is planar as evident in the nearly equal bond distances between metal atom and the ring carbons. The Ir–Cl bond distance is 2.398 Å, which is close to that in related iridium and rhodium complexes with two-coordinated chelating N,N′-based ligands [56]. An interesting structural feature of the homodinuclear complex [**8**]BF₄ is the presence of an orientational disorder for the location of the benzene ring C14–C19 (occupancy factor of 75). The ring C14–C19 is the major contribution of the disordered system, whereas the corresponding minor contribution is the orientational disorder ring C26–C31 (occupancy factor of 25) (not shown in Fig. 3). The refined site distribution of C14–19 to C26–31 is 75/25. The Ru(1)···Cl(1) 2.403(13) Å and Ru(2)···Cl(2) 2.4339(14) Å bond lengths are comparable to mononuclear complexes. However, the bond length of Ru(2)···Cl(2) is much longer than the other metal to chloride Ru(1)···Cl(1) distance despite there being no significant change in their environments.

6. Conclusion

The 3,5-bis(2-pyridyl)pyrazole (bpp-H) ligand, which posses two contiguous binding sites for metal ions, has been found to form mono- and binuclear complexes with metal precursors. However, arene ruthenium complexes yielded bimetallic complexes with bpp-H, whereas (η^5-C$_5$Me$_5$)M dimers and mononuclear triphenylphosphine complexes do not yield bimetallic complexes with bpp-H, and this could be due to the steric effect of the η^5-C$_5$Me$_5$ and PPh$_3$ ligands. The mononuclear complexes can be made available to bind with other less steric metal precursors to form homo or hetero bimetallic complexes through the other two nitrogen atoms of bpp-H and this work is still in progress and will be reported in the near future.

Appendix A. Supplementary data

CCDC 700916, 702728 and 702729 contain the supplementary crystallographic data for [**1**]PF$_6$, [**5**]PF$_6 \cdot$ H$_2$O and [**8**]BF$_4 \cdot$ H$_2$O. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.12.050.

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