*J. Chem. Sci.* Vol. 126, No. 4, July 2014, pp. 1143–1151. 

# Synthesis and structural study of platinum group metal complexes containing pyrimidine bridged pyrazolyl-pyridine ligand and $\eta^5$ and $\eta^6$ – cyclic hydrocarbons

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MS received 22 October 2013; revised 28 May 2014; accepted 6 April 2014

**Abstract.** The mononuclear compounds [($\eta^6$-arene)Ru(*bppm*)Cl]$PF_6$ {*bppm* = 4,6-bis{3-(2-pyridyl)-1H-pyrazol-1-yl}pyrimidine; arene = $C_6H_6$, [**1**]; p-$^i$Pr$C_6H_4$Me, [**2**]; $C_6Me_6$, [**3**]}, [CpRu(*bppm*)($PPh_3$)]$PF_6$ {Cp = $\eta^5$-$C_5H_5$, [**4**]; $\eta^5$-$C_5Me_5$, [5]; $\eta^5$-$C_9H_7$, [**6**]} and [Cp*M(*bppm*)Cl]$PF_6$ {M = Rh [**7**]; Ir [**8**]} have been synthesized from the reaction of 4,6-bis{3-(2-pyridyl)-1H-pyrazol-1-yl}pyrimidine (*bppm*) and the corresponding precursor metal complexes [($\eta^6$-arene)Ru($\mu$-Cl)Cl]$_2$, [CpRu($PPh_3$)$_2$Cl] and [Cp*M($\mu$-Cl)Cl]$_2$, respectively, in the presence of $NH_4PF_6$. They were characterized by the following techniques viz. IR, NMR, mass spectrometry and UV-visible spectroscopy. The molecular structures of [**2**] and [**7**] have been established by single crystal X-ray structure analyses.

**Keywords.** Arene-ligands; 4,6-bis{3-(2-pyridyl)-1H-pyrazol-1-yl}pyrimidine; Ruthenium; Rhodium; Iridium.

## 1. Introduction

There are a number of publications related to the chemistry of transition metals associated with polypyridine ligands containing sp$^2$-hybridised nitrogen atoms.[1–4] The charge transfer properties of these compounds justify the interest in this field. It is noted that polypyridines also play an important role in building up the inorganic architectures.[5–7] In recent years, specially designed ligands consisting of a pyrimidine[8–10] molecule bearing one or more pyrazolyl substituents have been effectively used to coordinate the metallic fragments. These compounds offer a good scope to study fluxional processes, electronic, magnetic, and photonic devices that are available from various self-assembly techniques.[11,12] Besides these compounds, the organometallic compounds of $\eta^6$-arene ruthenium,[13,14] and Cp* rhodium and iridium have generated considerable interest in the area of research as potential anti-cancer agents.[15–19]

The ligand 4,6-bis{3-(2-pyridyl)-1H-pyrazol-1-yl} pyrimidine (*bppm*) and its analogue, 4,6-bis{3-(2-pyridyl)-1H-pyrazol-1-yl}pyridazine (*bppp*), have a structural similarity. The *bppp* ligand has the ability to bind with two half-sandwich platinum group metal centers, resulting in dinuclear complexes.[20] In the case of ligand *bppp,* the pyridyl-pyrazole rings are bonded *para* to each other whereas in the case of ligand *bppm*, they are bonded *meta* to each other on central six membered ring. This ligand can coordinate the metals by a number of ways yielding mono and dinuclear compounds. It can also coordinate through pyridine and pyrazolyl nitrogens or nitrogens of pyrimidine and pyrazolyl group to form mono and dinuclear complexes. However, in the present work, only mononuclear complexes were isolated by coordination through pyridine and pyrazolyl nitrogens.

In recent years, half-sandwich platinum group metal complexes with a variety of nitrogen-based ligands[21–27] including pyridyl-pyridazine, thiazolyl-pyridine and pyrazolyl-pyridazine ligands have been carried out. The ruthenium complexes of these types of nitrogen-based ligands have a capacity to function as catalysts for the oxidation of water to oxygen.[28,29] Although extensive studies have been made on ruthenium complexes containing polypyridyl ligands, complexes containing polydentate 4,6-bis{3-(2-pyridyl)-1H-pyrazol-1-yl}pyrimidine (*bppm*) ligand have not been investigated.

The present communication deals with the synthetic methodology applied for the development of homogeneous and immobilized half-sandwich ruthenium, rhodium and iridium complexes bearing 4,6-bis{3-(2-

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pyridyl)-1H-pyrazol-1-yl}pyrimidine (*bppm*), as specific *N,N*-bidentate chelating ligand (chart 1).

## 2. Experimental

### 2.1 *General remarks*

All the solvents were dried and distilled prior to use. 4,6-dichloropyrimidine (Aldrich) was procured and used as received. $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl]_2$, $[(\eta^6\text{-}p\text{-}^i PrC_6H_4Me)Ru(\mu\text{-}Cl)Cl]_2$, $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}Cl)Cl]_2$,[30] [Cp*M$(\mu\text{-}Cl)Cl]_2$ (M = Rh, Ir),[31] [CpRu$(PPh_3)_2Cl$], [Cp*Ru$(PPh_3)_2Cl$] and $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ were prepared according to the methods in literature. The 3-(2-pyridyl)-1H-pyrazole[32] and 4,6-bis{3-(2-pyridyl)-1H-pyrazol-1-yl}pyrimidine (*bppm*)[33] were prepared by using the method described earlier. $^1$H-NMR spectra were recorded on Bruker AMX-400 MHz spectrometer and infrared spectra were recorded on Perkin-Elmer 983 spectrophotometer with samples prepared as KBr pellets. Elemental analyses of the complexes were carried out using Perkin-Elmer-2400 CHN/S series. Mass spectra were obtained from Waters ZQ-4000 mass spectrometer by ESI method. Absorption spectra were obtained at room temperature using a Perkin-Elmer Lambda 25 UV/visible spectrophotometer.

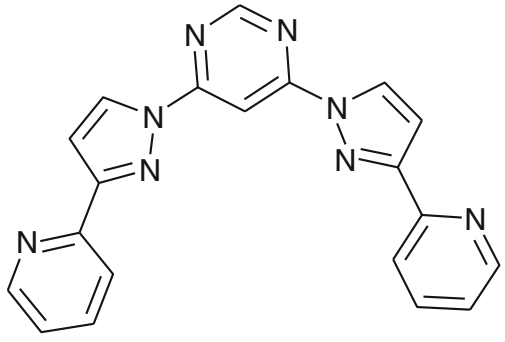
### 2.2 *Single crystal x-ray structure analyses*

X-ray quality crystals of complexes [**2**] and [**7**] were grown by slow diffusion of hexane in dichloromethane/acetonitrile solution of [**2**] and [**7**]. The x-ray intensity data were measured at 293(2) K on a Bruker Apex II CCD area detector employing graphite monochromated with Mo-$K\alpha$ radiation ($\lambda$ = 0.71073 Å). An empirical absorption correction was made by modeling a transmission surface by spherical harmonics employing equivalent reflections with $I>2\sigma(I)$ using the program SADBAS[34] and the structures were solved by direct methods using the program SHELXS 97[35] and refined by full matrix least squares base on $F_2$ using the program SHELXL-97.[36] The weighing system used followed the relationship $W = 1/[\sigma 2(F_{02})+0.0311P_2+3.5016\ P]$ where $P = (F_{02}+2F_{c2})/3$. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a 'riding' model. The refinement was converged at a final R = 0.0530 and 0.0372 (for complexes [**2**] and [**7**] respectively, for observed data $F_2$), and $wR_2$ = 0.0637 and 0.0425 (for complexes [**2**] and [7] respectively, for unique data $F_2$). Details of crystallographic data collection parameters and refinement are summarized in table 1 whereas selected bond lengths and angles are tabulated in table 2. The GOF values for the compounds are far away from unity. While the data for compound 7 were collected till higher angles, there were no reflections beyond $2\theta = 40°$. While collecting at low temperature can extend the $2\theta$ range, the instrument used is not equipped with a LT unit. The collection time was doubled to gain intensities, however the usable $2\theta$ range was limited to 40°. The N(1), N(6), N(9), and C(17) ellipsoids are 'flattened', but they are positively defined and do not undermine the quality of the structure.

There is an ambiguity in assigning N(8) and C(17). Exchanging the atoms did not improve the refinement. The labeling was done in analogy with other compounds and represents the most probable orientation of the molecular fragment.

The two atoms C(31) and N(9) have been included in the model without explanation in the text nor has a moiety formula been inserted in the cif. This is an attempt to model the solvent as an acetonitrile molecule. Now the central atom with occupancy of 0.5 is carbon of acetonitrile. Since the solvent molecule is acetonitrile, the two heavy peripheral atoms are N and C. It appears that we cannot differentiate between N and C, which can be due to the random orientation of N and C (they exchange the sites). We also could not locate the H atoms associated with the peripheral C atom. This peripheral site was treated as a 50/50 mixture of C and N, which considering the occupancy of this site yields one molecule of acetonitrile (per two molecules of the complex). The distance between the central C atom and peripheral atoms is 1.55 ang. While other solvent molecules may be present, only acetonitrile molecule has been located from the residual density map. Its presence was manifested by a large residual density, and its introduction lowered the R value from 5.55 to 4.43%.

There were no detectable reflections beyond $2\theta$ = 50° for compund 2 (the collection time was further




*bppm*

**Chart 1.** Ligand *bppm* used in the study.

**Table 1.** Crystallographic and structural refinement parameters for complexes [**2**] and [**7**].

| Complex | [**2**] | [**7**] |
|---|---|---|
| Chemical formula | $C_{30}H_{28}Cl\ F_6N_8PRu$ | $C_{30}H_{29}ClF_6N_8PRh$ |
| Crystal system | Monoclinic | Triclinic |
| Space group | P2/n | P -1 |
| Crystal colour and shape | Plate, yellow | Plate, yellow |
| Crystal size (mm) | 0.28 × 0.15 × 0.09 | 0.22 × 0.14 × 0.12 |
| a (Å) | 10.830(2) | 8.4962(17) |
| b (Å) | 16.351(3) | 10.542(2) |
| c (Å) | 18.379(4) | 18.076(4) |
| $\alpha$ (°) | – | 85.91(3) |
| $\beta$ (°) | 99.45(3) | 82.53(3) |
| $\gamma$ (°) | – | 83.89(3) |
| V (Å$^3$) | 3210.3(11) | 1593.5(6) |
| Z | 4 | 2 |
| T (K) | 293 (2) | 293 (2) |
| $D_x$ (g /cm$^3$) | 1.618 | 1.636 |
| $\mu$ (mm$^{-1}$) | 0.692 | 0.741 |
| Scan range (°) | 1.68<$\theta$<24.23 | 1.14<$\theta$<22.73 |
| Unique reflections | 4993 | 4047 |
| Reflections used [I>2$\sigma$(I)] | 1457 | 1771 |
| $R_{\text{int}}$ | 0.193 | 0.093 |
| Final R indices [I>2$\sigma$(I)] | 0.0530,$wR_2$ 0.0637 | 0.0372,$wR_2$ 0.0425 |
| R indices (all data) | 0.0878,$wR_2$0.2087 | 0.0543,$wR_2$ 0.1096 |
| Goodness-of-fit | 0.600 | 0.486 |
| Max, Min $\Delta\rho$ (e Å$^{-3}$) | 0.53, −0.50 | 0.39, −0.31 |

doubled as compared to compound 7). The maximum $2\theta$ range in the attached frame is 50.5°, and as seen there are no reflections at that angle. Because of the absence of the high-angle data and relatively poor crystal quality, we believe that the rigid body approach is a good and reliable refinement strategy which does not undermine the structural results.

### 2.3 *General procedure for the preparation of mononuclear compounds [1] to [3]*

A mixture of [($\eta^6$-arene)Ru($\mu$-Cl)Cl]$_2$ (arene = $C_6H_6$, *p*-$^i$Pr$C_6H_4$Me and $C_6Me_6$) (0.07 mmol), ligand *bppm* (0.15 mmol) and 2.5 equivalents of $NH_4PF_6$in dry methanol (15 mL) was stirred at room temperature for

**Table 2.** Selected bond lengths (Å) and angles (°) for complexes [**2**] and [**7**].

| [**2**]$PF_6$ | | [**7**]$PF_6$ | |
|---|---|---|---|
| *Interatomic distances (Å)* | | | |
| Ru-N1 | 2.107(5) | Rh-N1 | 2.122(5) |
| Ru-N2 | 2.109(4) | Rh-N2 | 2.183(5) |
| Ru-Cl1 | 2.383(3) | Rh-Cl1 | 2.393(2) |
| Ru-centroid ($C_6$ring) | 1.677 | Rh-centroid ($C_5$ ring) | 1.790 |
| C5-C6 | 1.347(6) | C5-C6 | 1.442(2) |
| N1-C1 | 1.390(5) | N1-C1 | 1.322(7) |
| *Angles* (°) | | | |
| N1-Ru-N2 | 74.3(2) | N1-Rh-N2 | 76.0 (2) |
| N1-Ru-Cl1 | 84.3(17) | N1-Rh-Cl1 | 85.9(16) |
| N2-Ru-Cl1 | 87.1(19) | N2-Rh-Cl1 | 88.2(17) |
| Ru1-N1-C5 | 117.3(3) | Rh1-N1-C5 | 116.4(5) |
| Ru1-N2-C6 | 115.1(4) | Rh1-N2-C6 | 112.5(4) |

6 h. The precipitate that formed was separated by filtration. The precipitate was washed with cold methanol and diethyl ether to remove excess ligand and dried *in vacuum*.

2.3a *[($\eta^6$-$C_6H_6$)Ru(bppm)Cl]$PF_6$[**1**]*: Brown color, Yield 85 mg (84%), $^1$H NMR (400 MHz, $CD_3CN$, $\delta$): 9.02 (d, 1H, $J$ = 6.0 Hz), 8.80 (s, 1H), 8.69 (s, 1H), 8.52 (dt, 2H, $J$ = 3.6 Hz), 8.31 (d, 1H, $J$ = 2.4 Hz), 8.19 (d, 1H, $J$ = 6.8 Hz), 7.95 (dt, 1H, $J$ = 1.8 Hz), 7.81 (d, 1H, $J$ = 5.2 Hz), 7.45 (dt, 1H, $J$ = 4.20 Hz), 7.34 (dt, 1H, $J$ = 2.8 Hz), 7.22 (d, 1H, $J$ = 3.2 Hz), 6.95 (dt, 1H, $J$ = 6.4 Hz), 6.81 (d, 1H, $J$ = 1.4 Hz), 5.87 (s, 6H, $C_6H_6$); Anal. Calc. for $C_{26}H_{20}ClN_8RuPF_6$ (725.9): C, 43.01; H, 2.78; N 15.43. Found: C, 42.89; H, 2.87; N, 15.28%; IR (KBr, cm$^{-1}$): 1585 ($\nu_{C=N}$), 839 ($\nu_{P-F}$), 559 ($\delta_{P-F}$); ESI-MS: 580.9 [M$^+$], 545.2 [M - Cl]; UV–Vis {acetonitrile, $\lambda_{max}$ nm ($\varepsilon$ $10^{-5}$ M$^{-1}$ cm$^{-1}$)}: 276 (0.57), 314 (0.92), 417 (0.04).

2.3b *[($\eta^6$-*p*-$^i$PrC$_6$H$_4$Me)Ru(bppm)Cl]$PF_6$[**2**]*: Orange-yellow solid, Yield 89 mg (83%); $^1$H NMR (400 MHz, $CD_3CN$, $\delta$): 9.22 (d, 1H, $J$ = 5.6 Hz), 8.82 (s, 1H), 8.73 (s, 1H), 8.55 (dt, 2H, $J$ = 1.8 Hz), 8.38 (d, 1H, $J$ = 2.8 Hz), 8.21 (d, 1H, $J$ = 6.8 Hz), 8.025 (dt, 1H, $J$ = 1.8 Hz), 7.78 (d, 1H, $J$ = 5.2 Hz), 7.48 (dt, 1H, $J$ = 4.2 Hz), 7.38 (dt, 1H, $J$ = 2.0 Hz), 7.25 (d, 1H, $J$ = 3.2 Hz), 6.95 (dt, 1H, $J$ = 6.4 Hz), 6.81 (d, 1H, $J$ = 1.4 Hz), 5.71 (d, 1H, $J$ = 6.0 Hz, $Ar_{p-cy}$), 5.64 (d, 1H, $J$ = 6.0 Hz, $Ar_{p-cy}$), 5.52 (d, 1H, $J$ = 5.6 Hz, $Ar_{p-cy}$), 5.39 (d, 1H, $J$ = 6.0 Hz, $Ar_{p-cy}$), 2.77 (sept, 1H, $CH(CH_3)_2$), 2.17 (s, 3H, $Ar_{p-cy}$-Me), 1.35 (d, 3H, $J$ = 3.2 Hz, $CH(CH_3)_2$), 1.35 (d, 3H, $J$ = 3.2 Hz, $CH(CH_3)_2$); Anal. Calc. for $C_{30}H_{28}ClN_8RuPF_6$ (782.1): C, 46.07; H, 3.61; N, 14.33. Found: C, 45.97; H, 3.68; N, 14.17%; IR (KBr, cm$^{-1}$): 1589 ($\nu_{C=N}$), 843 ($\nu_{P-F}$), 558 ($\delta_{P-F}$); ESI-MS: 637.1 [M$^+$], 602.1 [M - Cl]; UV–Vis {acetonitrile, $\lambda_{max}$ nm ($\varepsilon$ $10^{-5}$ M$^{-1}$ cm$^{-1}$)}: 274 (0.57), 313 (0.89), 418 (0.05).

2.3c *[($\eta^6$-$C_6Me_6$)Ru(bppm)Cl]$PF_6$[**3**]*: Brown color, Yield 85 mg (84%); $^1$H NMR (400 MHz, $CD_3CN$, $\delta$): 9.35 (d, 1H, $J$ = 6.0 Hz), 8.85 (s, 1H), 8.71 (s, 1H), 8.55 (dt, 2H, $J$ = 3.6 Hz), 8.32 (d, 1H, $J$ = 2.4 Hz), 8.27 (d, 1H, $J$ = 6.8 Hz), 7.95 (dt, 1H, $J$ = 1.8 Hz), 7.81 (d, 1H, $J$ = 5.2 Hz), 7.46 (dt, 1H, $J$ = 4.20 Hz), 7.34 (dt, 1H, $J$ = 2.8 Hz), 7.25 (d, 1H, $J$ = 3.2 Hz), 6.96 (dt, 1H, $J$ = 6.4 Hz), 6.82 (d, 1H, $J$ = 1.4 Hz), 2.21 (s, 18H, $C_6Me_6$); Anal. Calc. for $C_{32}H_{32}ClN_8RuPF_6$ (810.14): C, 47.44; H, 3.98; N, 13.83. Found: C, 46.13; H, 3.99; N, 13.76%; IR (KBr, cm$^{-1}$): 1602($\nu_{C=N}$), 844 ($\nu_{P-F}$), 558 ($\delta_{P-F}$); ESI-MS: 665.1 [M$^+$], 630.2 [M -Cl]; UV–Vis {acetonitrile, $\lambda_{max}$ nm ($\varepsilon 10^{-5}$M$^{-1}$ cm$^{-1}$)}: 276 (0.15), 325 (0.28), 419 (0.04).

2.4 *General procedure for the preparation of mononuclear compounds [**4**] to [**6**]*

A mixture of [CpRu($PPh_3$)$_2$Cl] (Cp = $C_5H_5$, $C_5Me_5$, $C_9H_7$) (0.1 mmol), ligand *bppm* (0.12 mmol) and 1.5 equivalents of $NH_4PF_6$ in dry ethanol (15 mL) was refluxed for 10 hours. The solution was changed from yellow to dark red. The solvent was evaporated on rotary evaporator and the residue was dissolved in dichloromethane and filtered to remove ammonium chloride and the filtrate was evaporated to 2 mL and excess hexane was added to develop dark brown precipitate.

2.4a *[CpRu(bppm)($PPh_3$)]$PF_6$ [**4**]*: Orange colour, yield 60 mg (73%); $^1$H NMR (400 MHz, $CDCl_3$, $\delta$): 9.07 (d, 1H, $J$ = 5.6 Hz), 8.82 (s, 1H), 8.71 (s, 1H), 8.51 (dt, 2H, $J$ = 2.4 Hz), 8.32 (d, 1H, $J$ = 2.8 Hz), 8.20 (d, 1H, $J$ = 5.4 Hz), 7.95 (dt, 1H, $J$ = 1.8 Hz), 7.82 (d, 1H, $J$ = 5.2 Hz), 7.45–7.22 (m, 18H), 6.95 (dt, 1H, $J$ = 6.4 Hz), 6.81 (d, 1H, $J$ = 1.4 Hz), 4.63 (s, 5H, $C_5H_5$); $^{31}$P {$^1$H} ($CDCl_3$, $\delta$): 49.34; Anal. Calc. for $C_{43}H_{34}N_8RuP_2F_6$ (939.79): C, 54.95; H, 3.65; N, 11.92. Found: C, 54.77; H, 3.68; N, 11.67%; IR (KBr, cm$^{-1}$): 1595($\nu_{C=N}$), 841 ($\nu_{P-F}$), 555 ($\delta_{P-F}$); ESI-MS: 794.1 [M$^+$]; UV–Vis {acetonitrile, $\lambda_{max}$ nm ($\varepsilon 10^{-5}$ M$^{-1}$ cm$^{-1}$)}: 276 (0.57), 314 (0.92), 417 (0.04).

2.4b *[Cp*Ru(bppm)($PPh_3$)]$PF_6$[**5**]*: Orange colour, yield 68 mg (76%); $^1$H NMR (400 MHz, $CDCl_3$, $\delta$): 9.27 (d, 1H, $J$ = 5.4 Hz), 9.18 (s, 1H), 9.03 (d, 1H, $J$ = 4.4 Hz), 8.94 (s, 1H), 8.84 (d, 1H, $J$ = 5.6 Hz), 8.68 (d, 1H, $J$ = 5.6 Hz), 8.53(d, 1H, $J$ = 6.4 Hz), 8.40 (t, 1H, $J$ = 3.6 Hz), 7.96–7.85 (m, 4H), 7.47−7.22 (m, 17H) 2.01 (s, 15H, $C_5Me_5$); $^{31}$P{$^1$H} ($CDCl_3$, $\delta$): 48.54; Anal. Calc. for $C_{48}H_{44}N_8RuP_2F_6$ (1009.9): C, 57.08; H, 4.39; N, 11.10. Found: C, 56.97; H, 4.28; N, 11.07%; IR (KBr, cm$^{-1}$): $\nu_{(P-F)}$1601 ($\nu_{C=N}$), 844 ($\nu_{P-F}$), 559 ($\delta_{P-F}$); ESI-MS (m/z): 864.2 (100%) [M-$PF_6$]$^+$; UV–Vis {acetonitrile, $\lambda_{max}$ nm ($\varepsilon$ $10^{-5}$ M$^{-1}$ cm$^{-1}$)}: 277 (0.58), 314 (0.95), 423 (0.04).

2.4c *[($\eta^5$-$C_9H_7$)Ru(bppm)($PPh_3$)]$PF_6$ [**6**]*: Yellowish brown colour, yield 66 mg (76%); $^1$H NMR (400 MHz, $CDCl_3$, $\delta$): 9.07 (d, 1H, $J$ = 5.6 Hz), 8.82 (s, 1H), 8.71 (s, 1H), 8.51 (dt, 2H, $J$ = 2.4 Hz), 8.32 (d, 1H, $J$ = 2.8 Hz), 8.20 (d, 1H, $J$ = 5.4 Hz), 7.95 (dt, 1H,

$J$ = 1.8 Hz), 7.82 (d, 1H, $J$ = 5.2 Hz), 7.45–7.22 (m, 23H), 6.95 (dt, 1H, $J$ = 6.4 Hz), 6.81 (d, 1H, $J$ = 1.4 Hz),4.87(t, 1H), 4.71 (d, 2H); $^{31}$P {$^{1}$H} ($CDCl_3$, $\delta$): 54.42; Anal. Calc. for $C_{47}H_{36}N_8RuP_2F_6$ (989.85): C, 57.03; H, 3.67; N, 11.32. Found: C, 56.87; H, 3.70; N, 11.26%; IR (KBr, $cm^{-1}$): 1595 ($\nu_{C=N}$), 839 ($\nu_{P-F}$), 558 ($\delta_{P-F}$); ESI-MS: 844.2 [$M^+$]; UV–Vis {acetonitrile, $\lambda_{max}$ nm ($\varepsilon$ $10^{-5}$ $M^{-1}$ $cm^{-1}$)}: 278 (0.54), 318(0.84), 408 (0.06).

### 2.5 *General procedure for the preparation of mononuclear compounds [7] and [8]*

A mixture of [Cp*M($\mu$-Cl)Cl]$_2$ (M = Rh, Ir) (0.07 mmol), ligand *bppm*(0.15 mmol) and 2.5 equivalents of $NH_4PF_6$ in dry methanol (15 mL) was refluxed for 4 h. The reaction mixture was cooled over night at room temperature and during this time, a dark yellow crystalline compound was formed. It was separated by filtration, washed with cold methanol and diethyl ether to remove excess ligand and dried *in vacuum*.

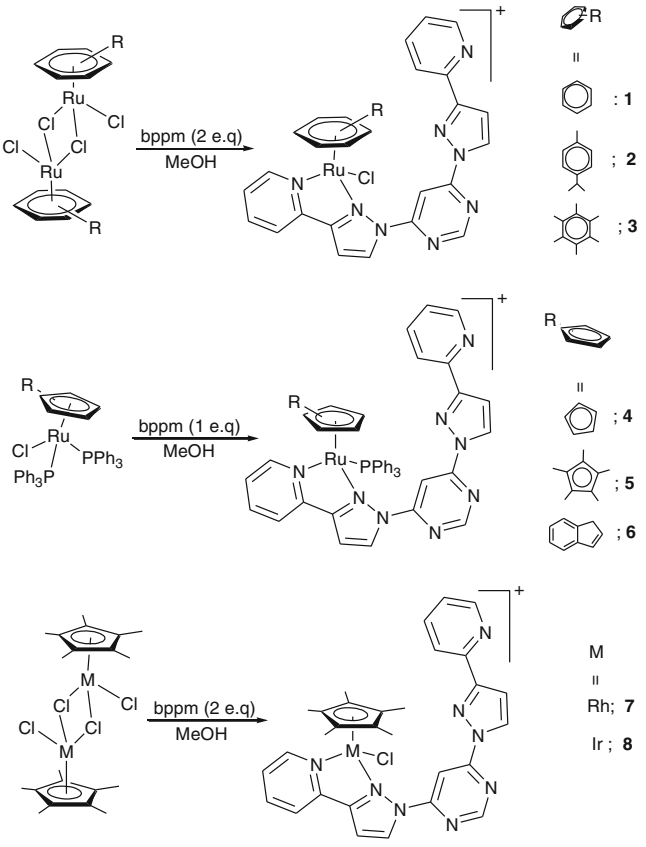
2.5a *[Cp*Rh(bppm)Cl]PF$_6$[7]*: Dark yellow in color, yield 96 mg (84%); $^{1}$H NMR (400 MHz, $CD_3CN$, $\delta$): 9.31 (d, 1H, $J$ = 5.2 Hz), 9.17 (d, 1H, $J$ = 4.40 Hz), 9.02 (d, 1H, $J$ = 4.4 Hz), 8.94 (s, 1H), 8.84 (d, 1H, $J$ = 5.6 Hz), 8.68 (d, 1H, $J$ = 5.6 Hz), 8.52 (d, 1H, $J$ = 7.2 Hz), 8.40 (t, 1H, $J$ = 3.6 Hz), 7.96–7.85 (m, 4H), 7.47 (t, 1H, $J$ = 5.6 Hz), 7.34 (d, 1H, $J$ = 3.6 Hz), 1.99 (s, 15H, $C_5Me_5$); Anal. Calc. For $C_{30}H_{29}ClN_8RhPF_6$ (784.93): C, 45.91; H, 3.72; N, 14.28; Found: C, 45.86; H, 3.76; N, 14.12%; IR (KBr, $cm^{-1}$): 1598 ($\nu_{C=N}$), 843 ($\nu_{P-F}$), 557 ($\delta_{P-F}$); ESI-MS (m/z): 639.2 (100%) [M–$PF_6$]$^+$; UV–Vis {acetonitrile, $\lambda_{max}$ nm ($\varepsilon$ $10^{-5}$ $M^{-1}$ $cm^{-1}$)}: 276 (0.39), 314 (0.67), 420 (0.04).

2.5b *[Cp*Ir(bppm)Cl]PF$_6$ [8]*: Dark yellow in color, yield 95 mg (83%); $^{1}$H NMR (400 MHz, $CD_3CN$, $\delta$): 9.27 (d, 1H, $J$ = 5.6 Hz), 9.15(s, 1H), 9.00 (d, 1H, $J$ = 4.2 Hz), 8.91 (s, 1H), 8.83 (d, 1H, $J$ = 5.6 Hz), 8.65 (d, 1H, $J$ = 5.2 Hz ), 8.51 (d, 1H, $J$ = 5.6 Hz), 8.40 (t, 1H, $J$ = 3.6 Hz ),7.90–7.81 (m, 4H), 7.41 (t, 1H, $J$ = 5.6 Hz), 7.34 (d, 1H, $J$ = 3.6 Hz), 1.77 (s, 15H, $C_5Me_5$); Anal. Calc. for $C_{30}H_{29}ClN_8IrPF_6$ (874.24): C, 41.22; H, 3.34; N, 12.82; Found: C, 41.12; H, 3.32; N, 12.73%; IR (KBr, $cm^{-1}$): 1601 ($\nu_{C=N}$), 844 ($\nu_{P-F}$), 558 ($\delta_{P-F}$); ESI-MS (m/z): 729.2 (100%) [M-$PF_6$]$^+$; UV–Vis {acetonitrile, $\lambda_{max}$ nm ($\varepsilon$ $10^{-5}$ $M^{-1}$ $cm^{-1}$)}: 277 (0.31), 314 (0.68), 423 (0.04).

## 3. Results and discussion

### 3.1 *Synthesis of the mononuclear compounds [1]–[8]*

The mononuclear cationic $\eta^5$- and $\eta^6$-cyclic hydrocarbons of ruthenium, rhodium and iridium complexes having 4,6-bis{3-(2-pyridyl)-1H-pyrazol-1-yl}pyrimidine (*bppm*) ligand *viz*., [($\eta^6$-$C_6H_6$)Ru(*bppm*)Cl]$PF_6$ [**1**], [($\eta^6$-*p*-$^{i}$Pr$C_6H_4$Me)Ru(*bppm*)Cl]$PF_6$ [**2**], [($\eta^6$-$C_6Me_6$)Ru(*bppm*)Cl]$PF_6$ [**3**], [CpRu(*bppm*)($PPh_3$)]$PF_6$ [**4**], [Cp*Ru(*bppm*)($PPh_3$)]$PF_6$[**5**], [($\eta^5$-$C_9H_7$)Ru(*bppm*)($PPh_3$)]$PF_6$ [**6**] [Cp*Rh(*bppm*)Cl]$PF_6$[**7**] and [Cp*Ir(*bppm*)Cl]$PF_6$[**8**] (scheme 1) have been prepared by the reaction of corresponding complexes [($\eta^6$-arene)Ru($\mu$-Cl)Cl]$_2$ (arene = $C_6H_6$, *p*-$^{i}$Pr$C_6H_4$Me and $C_6Me_6$), [CpRu($PPh_3$)$_2$Cl] (Cp =$C_5H_5$,$C_5Me_5$ and $C_9H_7$) and [Cp*M($\mu$-Cl)Cl]$_2$(M = Rh and Ir) with appropriate equivalents of ligand 4,6-bis{3-(2-pyridyl)-1H-pyrazol-1-yl}pyrimidine (*bppm*) in ethanol. These complexes were isolated as their hexafluorophosphate salts. The compounds [**1**] to [**8**] are orange-red, non-hygroscopic, air-stable, shiny crystalline solids. They are found to be sparingly soluble in methanol, dichloromethane and chloroform, but soluble in acetone and acetonitrile. All




**Scheme 1.** Preparation of the mononuclear compounds **1**–**8**.

these complexes were fully characterized by IR, NMR and UV-visible and mass spectrometry.

In order to prepare the dinuclear complexes 2:1 metal to ligand or one fold metal to mononuclear complexes concentration was used, but they were not successful in either of the cases. This could be due to the steric strain from arene or pentamethylcyclopentadienyl ligands already present on the metal atoms or steric strain from bonded site to the unbounded site of the ligand.

### 3.2 *Characterization*

All these complexes gave satisfactory analyses for C, H and N recorded in the experimental part. The infrared spectra of the complexes [**1**] to **[8]** exhibits a strong band in the region of 1600 $cm^{-1}$, corresponding to the $\nu_{C=N}$ stretching vibrations of heterocycles, and also strong bands at 841 and 558 $cm^{-1}$, corresponding to the $\nu_{P-F}$ and $\delta_{P-F}$ stretching vibrations for the $PF_6$ counter anion.

The mass spectra of the complexes [**1**] to **[8]** exhibited the corresponding $[M]^+$molecular ion peaks m/z at 581, 637, 665, 794, 864, 844, 639 and 729, as well as stable molecular ion fragments.

The $^1$H NMR spectrum of free ligand 4,6-bis{3-(2-pyridyl)-1H-pyrazol-1-yl}pyrimidine (*bppm*) exhibit a characteristic set of eight resonances at $\delta$ 8.85 (d, 2H), 8.73 (s, 1H), 8.70 (d, 2H), 8.66 (s, 1H), 8.28 (d, 2H), 7.86 (dt, 2H), 7.43 (dt, 2H), 7.22 (d, 2H) for pyrazole, pyrimidine and pyridine ring protons. When coordinated with the metal atom, the cationic complexes [**1**] to**[8]** exhibit ten to thirteen distinct resonances at downfield region compared to free ligand, at $\delta$ 9.35 (d, 1H), 8.85 (s, 1H), 8.71 (s, 1H), 8.55–8.48 (dt, 2H), 8.32 (d, 1H), 8.27 (d, 1H), 7.95 (dt, 1H), 7.81 (d, 1H), 7.46 (dt, 1H), 7.34 (dt, 1H), 7.25 (d, 1H), 6.96 (dt, 1H) and 6.82 (d, 1H) which are assignable to pyrazolyl, pyrimidine and pyridyl ring protons of the 4,6-bis{3-(2-pyridyl)-1H-pyrazol-1-yl}pyrimidine (*bppm*) ligand, indicating formation of mononuclear complexes. Besides these signals, complexes [**1**] and [**3**] exhibit a singlet for the protons of the benzene ring and hexamethylbenzene at $\delta$ 6.50 and 2.28, respectively. The complex [**2**] exhibits two doublets in the range $\delta$ 1.71–1.69, as well as a septet at $\delta$ 2.77 for the protons of the isopropyl group and a singlet at $\delta$ 2.17 for the methyl protons of *p*-cymene ring. The four doublets observed at $\delta$ 5.71 correspond to the aromatic *p*-cymene ring CH protons. This unusual pattern is attributed to the diastereotopic methyl protons of the isopropyl group and aromatic protons of the *p*-cymene ligand since the ruthenium atom is stereogenic due to the coordination of four different ligand atoms and chiral nature of metal atom.[37–39] The complexes [**4**] and [**5**] exhibits singlets at $\delta$ 4.63 and 2.01 for the protons of cyclopentadienyl ligand and methyl protons of pentamethylcyclopentadienyl ligand, respectively. The complex [**6**] exhibits a characteristic set of three signals such as multiplet, triplet and doublet, for the protons of the indenyl ligand at $\delta$ 7.46, 4.87 and 4.71 respectively. The multiplet was observed for the protons of triphenylphosphine ligand in the range $\delta$ 7.22 to 7.55 for the complexes [**4**], [**5**] and [**6**], respectively. The complexes [**7**] and [**8**] exhibits a strong peak at $\delta$ 1.99 and 1.77 for pentamethylcyclopentadienyl ligand that shifts downfield when compared to the starting complexes.

The $^{31}$P NMR spectra of complexes [**4**], [**5**] and [**6**] exhibited single sharp peaks at $\delta$ 49.34, 48.54, and 54.42 respectively, downfield compared to precursors. This downfield chemical shift of phosphorus nucleus indicates the formation of cationic complexes.

### 3.3 *Crystal structure analysis of [($\eta^6$-p-$^i$PrC$_6$H$_4$Me)RuCl(bppm)]PF$_6$ [2] and [Cp* RhCl(bppm)]PF6 [7]*

The molecular structures of [($\eta^6$-*p*-$^i$PrC$_6$H$_4$Me)Ru(*bppm*)Cl]$PF_6$[**2**] and [Cp*Rh(*bppm*)Cl]$PF_6$[**7**] have been established by single-crystal X-ray structure analysis. Complex 2 crystallize in the space group P2/n with four crystallographially identical molecules (i.e., Z = 4) are found within monoclinic unit cell whereas two molecules of each occupying the triclinic unit cell (i.e., Z = 2) for complex 7 in the space group of P1. Both the complexes display a typical piano-stool geometry at the metal center coordinated by the aromatic ligand, chloride and a chelating *N,N′*-ligand (figures 1 and 2). The metal atom is in octahedral arrangement and the *bppm* ligand is found to coordinate through the N1 atom of the pyridine moiety and the N2 atom of the pyrazolyl ring generating a five-membered metallocycle

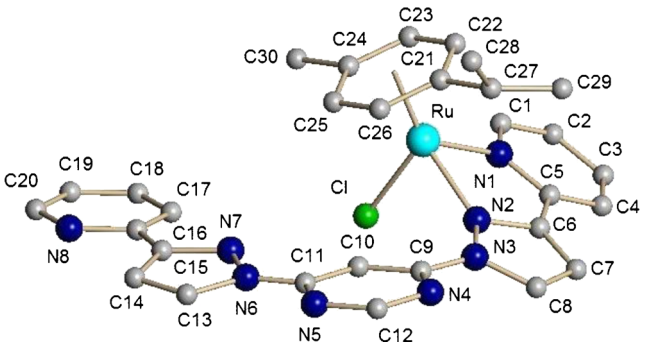



**Figure 1.** Molecular structure of complex **2**. Hydrogen atoms and anion are omitted for clarity.

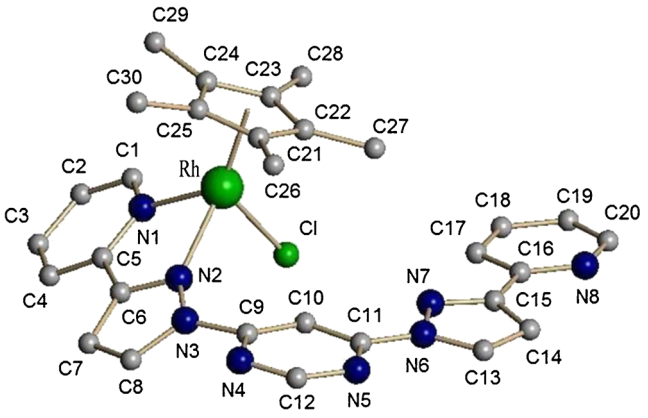



**Figure 2.** Molecular structure of complex **7**. All hydrogen atoms, solvent molecule and anion are omitted for clarity.

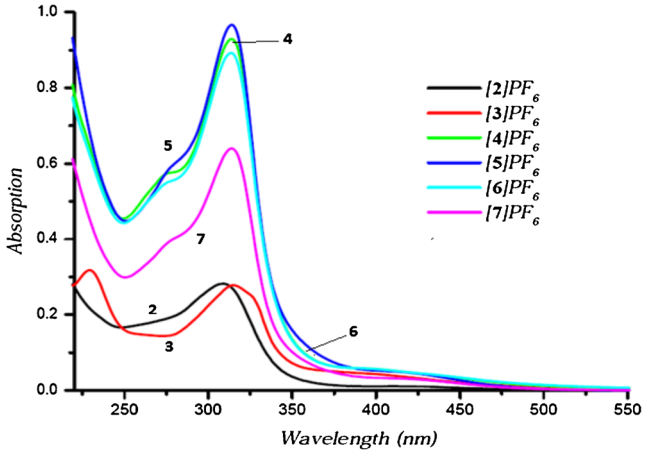



**Figure 3.** UV-visible electronic spectra of representative complexes in acetonitrile at 298 K.

(figures 1 and 2). In these complexes, the N atom of pyrimidine points away from the metal center and show no interaction with neighboring cations. The selected bond lengths and bond angles for the complexes [**2**] and [**7**] are presented in table 2.

In the mononuclear compounds [**2**] and [**7**] the N1-metal {2.107(5) and 2.122(5)Å}, distance of the pyridyl ring is slightly shorter than the corresponding pyrazolyl, N2-metal distance {2.109(4) and 2.183(5) Å}, which are comparable to those in $[(\eta^6\text{-}C_6Me_6)RuCl(C_5H_4N\text{-}2\text{-}CH{=}N{=}C_6H_4\text{-}p\text{-}NO_2)]PF_6$,[40] $[Ru(mes)Cl\{C_5H_4N\text{-}2\text{-}C(Me){=}N(CHMePh)\}]BF_4$,[41] $[Cp^*RhCl(C_5H_4N\text{-}2\text{-}CH{=}N{=}C_6H_4\text{-}p\text{-}NO_2)]BF_4$,[42] $[(\eta^6\text{-}C_6H_6)Ru(2\text{-}(2\text{-thiazolyl})\text{-}1,8\text{-naphthyridine})Cl]PF_6$,[37] and $[(\eta^6\text{-}p\text{-cymene})RuCl(2,3\text{-bis}(2\text{-Py})pyrazine)]\text{-}BF_4$.[43] While the M-Cl [2.383 (3) and 2.393(2)] bond lengths show no significant differences in all the cations and reported values.[44–46] The N(1)–M(1)–N(2) bond angle in complexes **2** and **7** is found to be [74.3(2)°] and [76.0(2)°] respectively, which are similar to those of complexes $[(\eta^6\text{-}p\text{-cymene})RuCl(2,3\text{-bis}(2\text{-Py})pyrazine)]^+$ and $[(\eta^6\text{-}p\text{-cymene})RuCl(2,3\text{-bis}(2\text{-Py})quinoxaline)]^+$.[47] The distance between the ruthenium atom and the centroid of the $(\eta^6\text{-}p\text{-}^i PrC_6H_4Me)$ ring is 1.677 Å in compound [**2**], whereas between the rhodium atom and the centroid of the Cp* ring it is 1.790 Å in compound [**7**]. These bond distances are comparable to those in the related complex cations $[(\eta^6\text{-}p\text{-cymene})Ru(pyNp)Cl]PF_6$, $[Cp^*Ir(pyNp)Cl]PF_6$ (PyNp=2-(2-Py)-1,8-naphthyridine) (1.79 Å)[37] and $[Cp^*Rh(3,6\text{-bis}(2\text{-Py})4\text{-phenylpyridazine})\text{-}Cl]PF_6$ (1.789 Å).

### 3.4 *UV-visible spectroscopy*

Electronic absorption spectra of compounds *bppm* and [**1**] to [**8**] were measured in acetonitrile at $10^{-5}$ M concentration in the range 220–550 nm and the spectral data are described in the experimental section. The spectrum of the ligand 4,6-bis{3-(2-pyridyl)-1H-pyrazol-1-yl}pyrimidine (*bppm*) exhibit two bands at 316 nm and 331 nm as shoulder peaks, which are assigned to intra-ligand $\pi \rightarrow \pi^*$ transitions. The electronic spectra of these complexes are characterized by two main features, *viz*., an intense ligand–localized or intra-ligand $\pi \rightarrow \pi^*$ transition in the ultraviolet region and metal-to-ligand charge transfer (MLCT) $d\pi(M) \rightarrow \pi^*$ (*bppm*-ligand) bands in the visible region.[48] Since the low spin $d^6$ configuration of the mononuclear complexes provides filled orbitals of proper symmetry at Ru(II), Rh(III) and Ir(III) centres, these can interact with low lying $\pi^*$ orbitals of the ligands. It is observed that all these complexes [**1**] to [**8**] display an intense band in the region 308-316 nm and a broad peak at 417-423 nm. The high intensity band in UV region for mononuclear complexes is assigned to inter and intra-ligand $\pi \rightarrow \pi^*/n \rightarrow \pi^*$transitions[49–51] while the low energy absorption band in the visible region for all complexes is assigned to metal-to-ligand charge transfer (MLCT) ($t_{2g} \rightarrow \pi^*$). The spectra of these complexes are represented in figure 3.

## 4. Conclusions

In this work, synthesis of novel platinum group metal complexes was undertaken in which the ligand *bppm* reacts with a series of arene ruthenium, Cp* rhodium, ruthenium and iridium complexes forming a novel series of mononuclear complexes. However, dimeric complexes were not obtained probably due to the steric crowding of the mononuclear compounds that prevents dimerization.

## Supplementary Information

CCDC-**752869** for [**2**] and CCDC-**752870** for [**7**] contain the supplementary crystallographic data of this work, that can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

## Acknowledgements

K M Rao is grateful to UGC and CSIR, New Delhi for the financial support received vide research grants No.F.No.39-793/2010 (SR) and 01(2493)/11/EMR-II, respectively.

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