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Mono and dinuclear half-sandwich platinum group metal complexes bearing pyrazolyl-pyrimidine ligands: Syntheses and structural studies

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A B S T R A C T

Reactions of 0.5 eq. of the dinuclear complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (arene = η^6-C_6H_6, η^6-*p*-$^iPrC_6H_4Me$) and $[(Cp^*)M(\mu\text{-}Cl)Cl]_2$ (M = Rh, Ir; Cp^* = η^5-C_5Me_5) with 4,6-disubstituted pyrazolyl-pyrimidine ligands (L) *viz.* 4,6-bis(pyrazolyl)pyrimidine (L1), 4,6-bis(3-methyl-pyrazolyl)pyrimidine (L2), 4,6-bis(3,5-dimethyl-pyrazolyl)pyrimidine (L3) lead to the formation of the cationic mononuclear complexes $[(\eta^6\text{-}C_6H_6)Ru(L)Cl]^+$ (L = L1, **1**; L2, **2**; L3, **3**), $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(L)Cl]^+$ (L = L1, **4**; L2, **5**; L3, **6**), $[(Cp^*)Rh(L)Cl]^+$ (L = L1, **7**; L2, **8**; L3, **9**) and $[(Cp^*)Ir(L)Cl]^+$ (L = L1, **10**; L2, **11**; L3, **12**), while reactions with 1.0 eq. of the dinuclear complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ and $[(Cp^*)M(\mu\text{-}Cl)Cl]_2$ give rise to the dicationic dinuclear complexes $[\{(\eta^6\text{-}C_6H_6)RuCl\}_2(L)]^{2+}$ (L = L1, **13**; L2, **14**; L3, **15**), $[\{(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)RuCl\}_2(L)]^{2+}$ (L = L1, **16**; L2, **17**; L3, **18**), $[\{(Cp^*)RhCl\}_2(L)]^{2+}$ (L = L1, **19**; L2, **20**; L3, **21**) and $[\{(Cp^*)IrCl\}_2(L)]^{2+}$ (L = L1 **22**; L2, **23**; L3 **24**). The molecular structures of [**3**]PF_6, [**6**]PF_6, [**7**]PF_6 and [**18**]$(PF_6)_2$ have been established by single crystal X-ray structure analysis.

Keywords
Arene, Cp^*, Pyrazolyl-pyrimidine, Ruthenium, Rhodium, Iridium

1. Introduction

During the last few decades there has been great interest in the chemistry of transition metals associated with polydentate ligands with sp^2-hybridized nitrogen atoms, for instance, polypyrazolylborates [1,2] and polypyridines [2–10]. In many cases the charge transfer properties of these compounds justify this interest. Especially with these nitrogen donor ligands have been shown to be effective catalysts for oxidation reactions [11–19] and for ring-opening metathesis polymerization [20] and recent studies of arene ruthenium complexes have shown that they are found to inhibit cancer cell growth [21–26], as non-linear optical (NLO) materials [27,28]. For a majority of the complexes studied, the metal centers are linked by a bridging ligand and the nature of the bridge has a fundamental influence on the electronic interaction between the metals and therefore on the characteristics of the material.

The ligand 4,6-bis(pyrazolyl)pyrimidine (L1) and its analogues, 4,6-bis(3-methyl-pyrazolyl)pyrimidine (L2) and 4,6-bis(3,5-dimethyl-pyrazolyl)pyrimidine (L3), are the subject of this investigation. They have a structural similarity to 3,6-bis(pyrazolyl)pyridazine (**A**) and 4,5-bis(pyrazolyl)quinoxaline (**B**) both of which have been previously studied [29,30]. In our previous work, we demonstrated that the ligand **A** does not yield dinuclear compounds with two half-sandwich platinum group metal atoms, since the steric nature of the ligand, resulted only in the formation of mononuclear complexes [29]. However it is true in the case of more sterically free ligand **B** also, because it also yielded mononuclear complexes, since the pyrazole rings of the ligand tilted with respect to the central quinoxaline ring because of the steric collide between the R' groups of the pyrazole rings. In the case of ligand **A** the pyrazolyl rings are bonded *para* to each other, where as in the case of ligand **B**, they are bonded *ortho* to each other on central six membered rings. But sterically less demanding ligand L (L1–L3) can coordinate to two half-sandwich platinum group metal centers, since the pyrazolyl rings of the ligand are bonded *meta* to each other, leading to reduced steric interaction, which enhances the stability of the dinuclear complexes.

In recent years, we have been carrying out arene ruthenium complexation reactions with a variety of nitrogen-based ligands [31–36] including pyridyl-pyridazine and pyrazolyl-pyridazine ligands. Ruthenium complexes of these types of nitrogen-based ligands have a capacity to function as catalysts for the oxidation of water to oxygen [37–39]. Although extensive studies have been made on ruthenium complexes containing polypyridyl ligands, complexes containing pyrazolyl-pyrimidine ligands have not yet been investigated.

In the present paper, we focus on the synthetic methodology applied for the development of homogeneous and immobilized half-sandwich ruthenium, rhodium and iridium complexes bearing bis(pyrazolyl)pyrimidine, as a specific *N,N*-bidentate bridging ligands (L) (Scheme 1).

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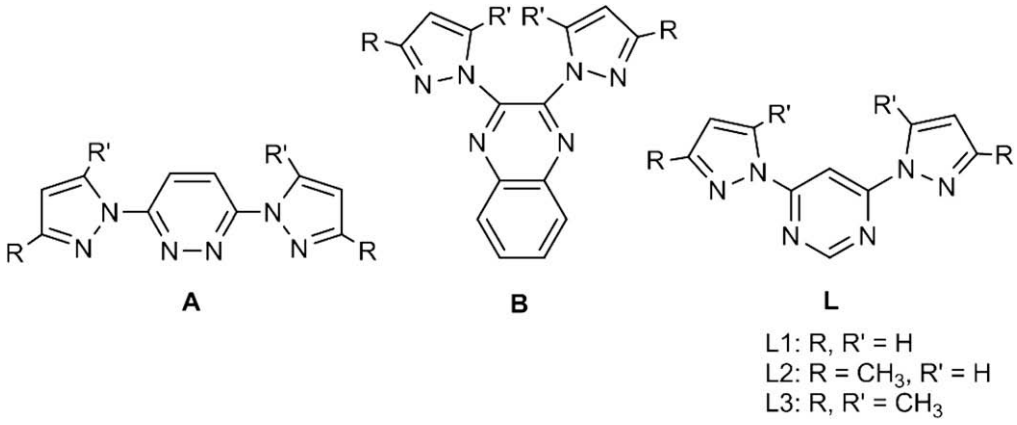


Scheme 1.

2. Experimental

2.1. General remarks

All solvents were dried and distilled prior to use. 3-methylpyrazole, 3,5-dimethylpyrazole and 4,6-dichloropyrimidine (Aldrich) were purchased and used as received. $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl]_2$, $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(\mu\text{-}Cl)Cl]_2$ [40–42], and $[(Cp^*)M(\mu\text{-}Cl)Cl]_2$ (M = Rh, Ir) [43–45] were prepared according to literature methods. The preparation of ligand 4,6-bis(pyrazolyl)pyrimidine (L1) has been previously described [46] and ligand 4,6-bis(3,5-dimethyl-pyrazolyl)pyrimidine (L3) was prepared by the modified procedure of Oro et al. [47]. ^{1}H NMR spectra were recorded on Bruker AMX-400 MHz spectrometer. Infrared spectra were recorded as KBr pellets on a Perkin–Elmer 983 spectrophotometer; elemental analyses of the complexes were performed on a Perkin–Elmer-2400 CHN/S analyzer. 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–Vis spectrophotometer.

2.2. Single crystal X-ray structure analyses

Crystals suitable for X-ray diffraction study for compounds [3]PF_6, [**6**]PF_6, [**7**]PF_6 and [**18**]$(PF_6)_2$ were grown by slow diffusion of diethylether/hexane into dichloromethane/acetone solution of complexes [**3**]$PF_6{\cdot}H_2O$, [**6**]PF_6, [**7**]PF_6 and [**18**]$(PF_6)_2{\cdot}H_2O$, respectively. The crystals were mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, using Mo Kα graphite monochromated radiation (λ = 0.71073 Å) with ϕ range 0–200°. The structures were solved by direct methods using the program SHELXS–97 [48]. Refinement and all further calculations were carried out using SHELXL–97 [49]. The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2. Crystallographic details are summarized in Table 1 and selected bond lengths and angles are presented in Table 2. Figs. 1–4 were drawn with ORTEP [50] and Fig. 5 with the software MERCURY [51,52].

2.3. Preparation of ligands (L2 and L3)

2.3.1. 4,6-Bis(3-methyl-pyrazolyl)pyrimidine (L2)

To a solution of 3-methylpyrazole (1.20 g, 14.7 mmol) in 50 ml of THF was added fine pieces of potassium (0.600 g, 15.3 mmol), the mixture was refluxed at 50 °C until the potassium was completely dissolved. Then 4,6-dichloropyrimidine (1.094 g, 7.35 mmol) was added to the reaction mixture(pale-brown solution), which was refluxed for 5 h. Then 80 ml of water was added and the solution refrigerated overnight. The colorless solid was filtered and washed with water (2 × 10 ml) and dried under P_2O_5. The pure compound was obtained after recrystallization from chloroform/hexane.

Yield: 0.72 g, 57.8%.

Elemental Anal. Calc. for $C_{12}H_{12}N_6$: C, 59.99; H, 5.03; N, 34.98. Found: C, 59.63; H, 5.18; N, 34.72%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.71 (s, 1H), 8.45 (d, 2H, ^3J = 2.4 Hz), 8.29 (s, 1H), 6.29 (d, 2H, ^3J = 2.4 Hz), 2.39 (s, 6H, CH_3); ESI-MS (*m/z*): 241.11 $[M+H]^+$; IR (KBr, cm^{-1}): 2924m, 1597s, 1464m, 1382m, 1211m, 1044s, 777s.

2.3.2. 4,6-Bis(3,5-dimethyl-pyrazolyl)pyrimidine (L3)

The L3 ligand was synthesized in a similar manner using 3,5-dimethylpyrazole (1.50 g, 15.6 mmol), potassium (0.60 g, 15.0 mmol) and 4,6-dichloropyrimidine (1.10 g, 7.35 mmol). However, after refluxing the THF solution for 5 h, the mixture was evaporated to dryness. The product was extracted three times with 30 ml of toluene. The solvent was removed, and the white solid obtained was dissolved in dichloromethane layering the resulting solution with hexane led to the precipitation of traces of pyrazole. L3 was obtained after filtration and evaporation to dryness of the resulting solution. The solid was recrystallized from chloroform/hexane.

Yield: 1.5 g, 55%.

Elemental Anal. Calc. for $C_{14}H_{16}N_6$: C, 62.67; H, 6.01; N, 31.32. Found: C, 62.68; H, 6.05; N, 31.28%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (s, 1H), 8.37 (s, 1H), 6.01 (s, 2H,), 2.67 (s, 6H, CH_3), 2.29 (s, 6H, CH_3); ESI-MS (*m/z*): 269.14 $[M+H]^+$); IR (KBr, cm^{-1}): 3446w, 2925m, 1593s, 1484s, 1385m, 1266m, 1019s, 771m.

2.4. General procedure for the preparation of the mononuclear complexes ***1–6***

A mixture of $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl]_2$ (arene = C_6H_6 and p-^{i}PrC_6H_4Me) (0.07 mmol), ligand L (L1, L2 or L3) (0.15 mmol) and 2.5 equivalents of NH_4PF_6 in dry methanol (15 ml) was stirred at room temperature for 8 h resulting in the precipitation of a dark yellow solid. The precipitate was separated by filtration, washed with cold methanol, diethyl ether and dried *in vacuo*.

2.4.1. $[(\eta^6\text{-}C_6H_6)Ru(L1)Cl]PF_6$ ([***1***]PF_6)

Yield: 66 mg, 82.5%.

Elemental Anal. Calc. for $C_{16}H_{14}N_6RuClPF_6$ (571.97): C, 33.61; H, 2.47; N, 14.70. Found: C, 33.73; H, 2.65; N, 13.98%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.56 (d, 1H, ^3J = 2.4 Hz), 8.75 (d, 1H,

Table 1
Details of the data collection and results of the structure refinement parameters for complexes [**3**]$PF_6{\cdot}H_2O$, [**6**]PF_6, [**7**]PF_6 and [**18**]$(PF_6)_2{\cdot}H_2O$.

Complex	[**3**]$PF_6{\cdot}H_2O$	[**6**]PF_6	[**7**]PF_6	[**18**]$(PF_6)_2{\cdot}H_2O$
Chemical formula	$C_{20}H_{22}ClF_6N_6OPRu$	$C_{24}H_{30}ClF_6N_6PRu$	$C_{20}H_{23}ClF_6N_6PRh$	$C_{34}H_{46}Cl_2F_{12}N_6OP_2Ru_2$
Formula weight	628.03	684.03	630.77	1117.75
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\,2_1/a$
Crystal color and shape	Orange blade	Red block	Red block	Orange block
Crystal size (mm)	0.25 × 0.12 × 0.12	0.28 × 0.28 × 0.18	0.50 × 0.26 × 0.15	0.21 × 0.18 × 0.13
a (Å)	8.4350(11)	8.4928(10)	7.5841(6)	17.1745(13)
b (Å)	9.1359(12)	12.1384(14)	11.2581(10)	13.5980(8)
c (Å)	16.328(2)	14.1361(16)	14.7304(12)	17.6465(11)
α (°)	91.340(2)	99.418(2)	74.056(2)	90.00
β (°)	92.071(2)	90.677(2)	88.015(2)	90.062(8)
γ (°)	105.129(2)	104.611(2)	88.408(2)	90.00
V (Å^3)	1213.2(3)	1389.0(3)	1208.39(17)	4121.1(5)
Z	2	2	2	4
T (K)	203(2)	203(2)	203(2)	173(2)
D_x (g /cm^3)	1.763	1.636	1.734	1.802
μ (mm^{-1})	0.895	0.785	0.952	1.033
Scan range (°)	2.31 < θ < 28.31	1.76 < θ < 32.38	1.88 < θ < 32.33	1.91 < θ < 26.08
Unique reflections	12 483	17 438	14 825	8096
Reflections used [$I > 2\sigma(I)$]	5998	9027	7813	5203
R_{int}	0.0260	0.0383	0.0244	0.0644
Final R indices [$I > 2\sigma(I)$]	0.0385, wR_2 0.1160	0.0513, wR_2 0.1368	0.0428, wR_2 = 0.1387	0.0379, wR_2 = 0.0791
R indices (all data)	0.0415, wR_2 0.1203	0.0615, wR_2 0.1471	0.0463, wR_2 = 0.1437	0.0700, wR_2 = 0.0862
Goodness-of-fit (GOF)	1.186	1.121	1.178	0.849
Maximum, Minimum $\Delta\rho$ (e Å^{-3})	1.183, −0.564	1.128, −0.754	1.214, −1.051	0.949, −0.807

Table 2
Selected bond lengths and angles for complexes [**3**]$PF_6{\cdot}H_2O$, [**6**]PF_6, [**7**]PF_6 and [**18**]$(PF_6)_2{\cdot}H_2O$.

	[**3**]PF_6	[**6**]PF_6	[**7**]PF_6	[**18**]$(PF_6)_2$
Distances (Å)				
M1–Cl1	2.402(7)	2.388(8)	2.40(6)	2.393(1)
M2–Cl2	–	–	–	2.391(1)
M1–N1	2.076(2)	2.102(2)	2.106(2)	2.072(3)
M1–N3	2.092(2)	2.093(2)	2.138(2)	2.092(3)
M2–N4	–	–	–	2.092(3)
M2–N6	–	–	–	2.076(3)
M1–centroid[a]	1.690	1.685	1.770	1.685
M2–centroid[a]	–	–	–	1.678
Angles (°)				
N1–M1–N3	75.33(7)	75.56(9)	75.34(8)	75.70(1)
N4–M2–N6	–	–	–	75.0(1)
N1–M1–Cl1	84.76(6)	87.51(7)	90.43(7)	82.86(3)
N4–M2–Cl2	–	–	–	84.26(9)
N3–M1–Cl1	84.09(6)	84.27(7)	84.73(6)	83.31(9)
N6–M2–Cl2	–	–	–	81.70(9)

[a] Calculated centroid-to-metal distances (η^6-C_6 or η^5-C_5 coordinated aromatic ring).

^3J = 2.4 Hz), 8.66 (d, 1H, ^3J = 7.6 Hz), 8.63 (d, 1H, ^3J = 7.6 Hz), 8.29 (s, 1H), 8.02 (s, 1H), 6.96 (dd, 1H, ^3J = 2.0 Hz), 6.67 (dd, 1H, ^3J = 1.6 Hz), 6.07 (s, 6H, C_6H_6); ESI-MS (*m/z*): 427.2 [M−PF_6]$^+$, 392.1 [M−PF_6-Cl]$^+$, 314.1 [M−PF_6-Cl-C_6H_6]$^+$; IR (KBr, cm^{-1}): 844s $\nu_{(P-F)}$, 1522m, 1558m, 1608s ($\nu_{C=N}$ L1), 2925m, 3446w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5}$M^{-1} cm^{-1})}: 246(0.16), 324(0.17), 381(0.25), 464(0.04).

*2.4.2. [(η^6-C_6H_6)Ru(L2)Cl] PF_6 ([**2**]PF_6)*

Yield: 62 mg, 74.6%.

Elemental Anal. Calc. for $C_{18}H_{18}N_6RuClPF_6$ (599.86): C, 39.91; H, 3.35; N, 15.51. Found: C, 40.22; H, 3.08; N, 14.92%. ^{1}H NMR (400 MHz, CD_3CN, 25 °C, TMS): δ = 9.15 (s, 1H), 8.54 (d, 1H, ^3J = 8.4 Hz), 8.09 (s, 1H), 7.50 (d, 1H, ^3J = 4.6 Hz), 7.21 (d, 1H, ^3J = 4.6 Hz), 6.92 (d, 1H, ^3J = 2.8 Hz), 6.24 (s, 6H, C_6H_6), 2.83 (s, 3H, CH_3), 2.76 (s, 3H, CH_3); ESI-MS (*m/z*): 455.2 [M−PF_6]$^+$, 419.2 [M−PF_6-Cl]$^+$, 341.1 [M−PF_6-Cl-C_6H_6]$^+$; IR (KBr, cm^{-1}): 845s $\nu_{(P-F)}$, 1592m, 1558m, 1522m ($\nu_{C=N}$ L2), 2925m, 3434w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5}$M^{-1} cm^{-1})}: 319(0.23), 345(0.18), 456(0.04).

*2.4.3. [(η^6-C_6H_6)Ru(L3)Cl]PF_6 ([**3**]PF_6)*

Yield: 65 mg, 86.3%.

Elemental Anal. Calc. for $C_{20}H_{22}N_6RuClPF_6$ (628.03): C, 42.16; H, 3.89; N, 14.75. Found: C, 41.90; H, 4.05; N, 14.33%. ^{1}H NMR (400 MHz, CD_3CN): δ = 9.44 (s, 1H), 8.17 (s, 1H), 7.39 (s, 1H), 6.53 (s, 1H), 6.10 (s, 6H, C_6H_6), 2.82 (s, 3H, CH_3), 2.76 (s, 3H, CH_3), 2.75 (s, 3H, CH_3), 2.29 (s, 3H, CH_3); ESI-MS (*m/z*): 483.3 [M−PF_6]$^+$, 448.2 [M−PF_6-Cl]$^+$, 413.3 [M−PF_6−Cl−C_6H_6]$^+$; IR (KBr, cm^{-1}): 845s $\nu_{(P-F)}$, 1601m, 1560m, 1525m ($\nu_{C=N}$ L3), 2925m, 3482w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5}$M^{-1} cm^{-1})}: 273(0.15), 309(0.15), 354(0.25), 452(0.06).

*2.4.4. [(η^6-*p*-^{i}PrC_6H_4Me)Ru(L1)Cl]PF_6 ([**4**]PF_6)*

Yield: 65 mg, 75.5%.

Elemental Anal. Calc. for $C_{20}H_{22}N_6RuClPF_6$ (628.03): C, 38.26; H, 3.53; N, 13.38. Found: C, 37.92; H, 3.77; N, 12.95%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.48 (d, 1H, ^3J = 2.4 Hz), 8.77 (d, 1H, ^3J = 2.4 Hz, 1H), 8.67 (d, 1H, ^3J = 4.6 Hz), 8.61 (d, 1H, ^3J = 6.4 Hz), 8.29 (s, 1H), 7.97 (s, 1H), 6.96 (dd, 1H, ^3J = 2.0 Hz), 6.69 (dd, 1H, ^3J = 2.0 Hz), 6.04 (d, 1H, $^3J_{H,H}$ = 6.4 Hz, $Ar_{p\text{-}cy}$), 6.07 (d, 1H, ^3J = 6.4 Hz, $Ar_{p\text{-}cy}$), 5.99 (d, 1H, ^3J = 6.0 Hz, $Ar_{p\text{-}cy}$), 5.86 (d, 1H, ^3J = 6.0 Hz, $Ar_{p\text{-}cy}$), 2.74 (sept, 1H, ^3J = 6.2 Hz, $CH(CH_3)_2$), 2.18 (s, 3H, $Ar_{p\text{-}cy}$–Me), 1.14 (d, 3H, ^3J = 6.4 Hz, $CH(CH_3)_2$), 1.10 (d, 3H, ^3J = 7.6 Hz, $CH(CH_3)_2$); ESI-MS (*m/z*): 483.1 [M−PF_6]$^+$, 448.1 [M−PF_6-Cl]$^+$, 314.1 [M−PF_6-Cl-*p*-^{i}PrC_6H_4Me]$^+$; IR (KBr, cm^{-1}) 844s $\nu_{(P-F)}$, 1605m, 1557m, 1523m ($\nu_{C=N}$ L1), 3058m, 3489w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5}$M^{-1} cm^{-1})}: 286(0.65) 333(0.21), 436(0.02).

*2.4.5. [(η^6-*p*-^{i}PrC_6H_4Me)Ru(L2)Cl]PF_6 ([**5**]PF_6)*

Yield: 68 mg, 73.4%.

Elemental Anal. Calc. for $C_{22}H_{26}N_6RuClPF_6$ (651.06): C, 43.28; H, 4.29; N, 13.77. Found: C, 43.78; H, 3.94; N, 13.92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.25 (s, 1H), 8.48 (d, 1H, ^3J = 2.4 Hz), 7.89 (s, 1H), 7.78 (d, 1H, ^3J = 2.8 Hz), 6.70 (d, 1H, ^3J = 9.6 Hz), 6.39 (d, 1H, ^3J = 2.8 Hz), 5.98 (d, 2H, ^3J = 6.0 Hz, $Ar_{p\text{-}cy}$), 5.90 (d, 1H, ^3J = 6.0 Hz, $Ar_{p\text{-}cy}$), 5.86 (d, 1H, ^3J = 6.0 Hz, $Ar_{p\text{-}cy}$), 2.81 (s, 3H, CH_3), 2.75 (sept, 1H, $CH(CH_3)_2$), 2.38 (s, 3H, CH_3), 2.18 (s, 3H, $Ar_{p\text{-}cy}$–Me), 1.42 (d, 3H, ^3J = 3.2 Hz, $CH(CH_3)_2$), 1.17 (d, 3H, ^3J = 3.2 Hz,

$CH(CH_3)_2$); ESI-MS (*m/z*): 513.2 $[M-PF_6]^+$, 478.6 $[M-PF_6\text{-}Cl]^+$, 344.2 $[M-PF_6\text{-}Cl\text{-}p\text{-}^iPrC_6H_4Me]^+$; IR (KBr, cm^{-1}): 843s $\nu_{(P-F)}$, 1606m, 1560m, 1524m ($\nu_{C=N}$ L2), 2995m, 3447w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}$ cm^{-1})}: 294(0.36), 349(0.82), 470(0.02).

*2.4.6. [(η^6-p-$^iPrC_6H_4Me$)Ru(L3)Cl]PF_6 ([**6**]PF_6)*

Yield: 77 mg, 82.7%.

Elemental Anal. Calc. for $C_{24}H_{30}N_6RuClPF_6$ (684.09): C, 46.06; H, 4.83; N, 13.43. Found: C, 46.73; H, 4.25; N, 13.07%. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.44 (s, 1H), 8.11 (s, 1H), 7.32 (s, 1H), 7.05 (s, 1H), 5.96 (d, 1H, ^3J = 4.0 Hz, $Ar_{p\text{-}cy}$), 5.92 (d, 1H, ^3J = 3.2 Hz, $Ar_{p\text{-}cy}$), 5.84 (d, 1H, ^3J = 6.4 Hz, $Ar_{p\text{-}cy}$), 5.77 (d, 1H, ^3J = 6.4 Hz, $Ar_{p\text{-}cy}$), 2.81 (s, 3H, CH_3), 2.79 (s, 3H, CH_3), 2.81 (s, 3H, CH_3), 2.78 (s, 3H, CH_3), 2.49 (sept, 1H, $CH(CH_3)_2$), 2.17 (s, 3H, $Ar_{p\text{-}cy}$–Me), 1.09 (d, 3H, ^3J = 3.2 Hz, $CH(CH_3)_2$), 1.06 (d, 3H, ^3J = 3.2 Hz, $CH(CH_3)_2$); ESI-MS (*m/z*): 538.8 $[M-PF_6]^+$, 503.5 $[M-PF_6\text{-}Cl]^+$, 369.2 $[M-PF_6\text{-}Cl\text{-}p\text{-}^iPrC_6H_4Me]^+$; IR (KBr, cm^{-1}): 843s $\nu_{(P-F)}$, 1608m, 1560m, 1527m ($\nu_{C=N}$ L3), 3050m, 3447w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}$ cm^{-1})}: 287(0.38), 346(0.74), 477(0.08).

*2.5. General procedure for the preparation of the mononuclear complexes **7–12***

A mixture of $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (M = Rh and Ir) (0.08 mmol), ligand L (L1, L2 and L3) (0.17 mmol) and 2.5 equivalents of NH_4PF_6 in dry methanol (20 ml) was refluxed at 50 °C temperature for 4–6 h, resulting yellow color precipitation. The precipitate was separated by filtration, washed with cold methanol, diethyl ether and dried *in vacuo*.

2.5.1. [(Cp)Rh(L1)Cl]PF_6 ([**7**]PF_6)*

Yield: 73 mg, 77.8%.

Elemental Anal. Calc. for $C_{20}H_{23}N_6RhClPF_6$ (630.04): C, 38.08; H, 3.68; N, 13.98. Found: C, 38.13; H, 3.75; N, 13.91%. ^1H NMR (400 MHz, CD_3CN): δ = 9.01 (s, 1H), 8.84 (d, 1H, ^3J = 3.2 Hz), 8.66 (d, 1H, ^3J = 2.4 Hz), 8.33 (d, 1H, ^3J = 1.6 Hz), 8.31 (d, 1H, ^3J = 1.6 Hz), 7.98 (s, 1H), 7.02 (dd, 1H, ^3J = 1.6 Hz), 6.71 (dd, 1H, ^3J = 1.6 Hz), 1.75 (s, 15H, C_5Me_5); ESI-MS (*m/z*): 485.2 $[M-PF_6]^+$, 450.6 $[M-PF_6\text{-}Cl]^+$, 315.2 $[M-PF_6\text{-}Cl\text{-}Cp^*]$; IR (KBr, cm^{-1}): 844s $\nu_{(P-F)}$, 1606m, 1560m, 1524m ($\nu_{C=N}$ L1), 2999m, 3448w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}$ cm^{-1})}: 268(0.78), 286(0.76), 357(0. 4), 444(0.09).

2.5.2. [(Cp)Rh(L2)Cl]PF_6 ([**8**]PF_6)*

Yield: 65 mg, 62.5%.

Elemental Anal. Calc. for $C_{22}H_{27}N_6RhClPF_6$ (658.07): C, 35.32; H, 3.64; N, 11.23. Found: C, 35.26; H, 3.69; N, 11.21%. ^1H NMR (400 MHz, CD_3CN): δ = 8.78 (s, 1H), 8.43 (d, 1H, ^3J = 6.4 Hz), 8.09 (s, 1H), 6.76 (d, 1H, ^3J = 4.6 Hz), 6.40 (d, 1H, ^3J = 4.6 Hz), 6.32 (d, 1H, ^3J = 2.8 Hz), 2.70 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 1.77 (s, 15H, C_5Me_5); ESI-MS (*m/z*): 513.8 $[M-PF_6]^+$, 478.12 $[M-PF_6\text{-}Cl]^+$, 343.2 $[M-PF_6\text{-}Cl\text{-}Cp^*]$; IR (KBr, cm^{-1}): 845s $\nu_{(P-F)}$, 1598m, 1559m, 1521m ($\nu_{C=N}$ L2), 2995m, 3447w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}$ cm^{-1})}: 266(0.54), 301(0.45), 343(0.57), 452(0.07).

2.5.3. [(Cp)Rh(L3)Cl]PF_6 ([**9**]PF_6)*

Yield: 78 mg, 72%.

Elemental Anal. Calc. for $C_{24}H_{31}N_6RhClPF_6$ (686.87): C, 41.97; H, 4.55; N, 12.24. Found: C, 41.86; H, 4.65; N, 12.18%. ^1H NMR (400 MHz, CD_3CN): δ = 9.05 (s, 1H), 8.67 (s, 1H), 7.40 (s, 1H), 6.66 (s, 1H), 2.82 (s, 3H, CH_3), 2.76 (s, 3H, CH_3), 2.75 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.01 (s, 15H, C_5Me_5); ESI-MS (*m/z*): 541.81 $[M-PF_6]^+$, 506.6 $[M-PF_6\text{-}Cl]^+$, 371.2 $[M-PF_6\text{-}Cl\text{-}Cp^*]$; IR (KBr, cm^{-1}): 843s $\nu_{(P-F)}$, 1601m, 1557m, 1524m ($\nu_{C=N}$ L3), 3050m, 3434w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}$ cm^{-1})}: 261(0.09), 314(0.61), 441(0.05).

2.5.4. [(Cp)Ir(L1)Cl]PF_6 ([**10**]PF_6)*

Yield: 66 mg, 58.4%.

Elemental Anal. Calc. for $C_{20}H_{23}N_6IrClPF_6$ (720.09): C, 33.61; H, 2.47; N, 14.70. Found: C, 33.73; H, 2.65; N, 13.98%. ^1H NMR (400 MHz, CD_3CN): δ = 8.99 (s, 1H), 8.84 (d, 1H, ^3J = 3.2 Hz), 8.66 (d, 1H, ^3J = 2.4 Hz), 8.39 (d, 1H, $^3J_{H,H}$ = 1.6 Hz), 8.32 (d, 1H, $^3J_{H,H}$ = 1.6 Hz), 7.98 (s, 1H), 7.01 (dd, 1H, $^3J_{H,H}$ = 1.6 Hz), 6.70 (dd, 1H, $^3J_{H,H}$ = 2.0 Hz), 2.01 (s, 15H, C_5Me_5); ESI-MS (*m/z*): 575.2 $[M-PF_6]^+$, 535.6 $[M-PF_6\text{-}Cl]^+$, 400.2 $[M-PF_6\text{-}Cl\text{-}Cp^*]$; IR (KBr, cm^{-1}): 845s $\nu_{(P-F)}$, 1592m, 1558m, 1522m ($\nu_{C=N}$ L1) 2924m, 3439w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}$ cm^{-1})}: 279(0.53), 340(0.89), 402(0.20).

2.5.5. [(Cp)Ir(L2)Cl]PF_6 ([**11**]PF_6)*

Yield: 70 mg, 57.8%.

Elemental Anal. Calc. for $C_{22}H_{27}N_6IrClPF_6$ (748.13): C, 35.32; H, 3.64; N, 11.23. Found: C, 35.25; H, 3.68; N, 11.22%. ^1H NMR (400 MHz, CD_3CN): δ = 8.78 (s, 1H), 8.43 (d, 1H, ^3J = 6.4 Hz), 8.09 (s, 1H), 6.76 (d, 1H, ^3J = 4.6 Hz), 6.40 (d, 1H, ^3J = 4.6 Hz), 6.32 (d, 1H, ^3J = 2.8 Hz), 2.70 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 1.77 (s, 15H, C_5Me_5); ESI-MS (*m/z*): 603.1 $[M-PF_6]^+$, 568.2 $[M-PF_6\text{-}Cl]^+$, 433.2 $[M-PF_6\text{-}Cl\text{-}Cp^*]$; IR (KBr, cm^{-1}): 845s $\nu_{(P-F)}$, 1598m, 1559m, 1521m ($\nu_{C=N}$ L2), 2995m, 3446w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}$ cm^{-1})}: 267(0.54), 298(0.82), 429(0.08).

2.5.6. [(Cp)Ir(L3)Cl]PF_6 ([**12**]PF_6)*

Yield: 78 mg, 64.4%.

Elemental Anal. Calc. for $C_{24}H_{31}N_6IrClPF_6$ (776.96): C, 37.14; H, 4.03; N, 10.83. Found: C, 37.06; H, 4.05; N, 10.33%. ^1H NMR (400 MHz, CD_3CN): δ = 8.90 (s, 1H), 8.21 (s, 1H), 6.67 (s, 1H), 6.20 (s, 1H), 2.83 (s, 3H, CH_3), 2.76 (s, 3H, CH_3), 2.64 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.15 (s, 15H, C_5Me_5); ESI-MS (*m/z*): 631.2 $[M-PF_6]^+$, 596.6 $[M-PF_6\text{-}Cl]^+$, 461.2 $[M-PF_6\text{-}Cl\text{-}Cp^*]$; IR (KBr, cm^{-1}): 843s $\nu_{(P-F)}$, 1606m, 1560m, 1524m ($\nu_{C=N}$ L2), 3050m, 3446w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}$ cm^{-1})}: 268(0.50), 301(0.41), 361(0.51) and 464(0.04).

*2.6. General procedure for the preparation of the dinuclear complexes **13–18***

A mixture of $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (arene = C_6H_6 and η^6-p-$^iPrC_6H_4Me$) (0.1 mmol), ligand L (L1, L2 and L3) (0.1 mmol) and 2.5 equivalents of NH_4PF_6 in dry methanol (15 ml) was stirred at room temperature for 14 h resulting orange color precipitation. The precipitate was filtered, washed with cold methanol, diethyl ether and dried *in vacuo*.

*2.6.1. [{(η^6-C_6H_6)RuCl}$_2$(L1)]$(PF_6)_2$ ([**13**]$(PF_6)_2$)*

Yield: 72 mg, 77.4%.

Elemental Anal. Calc. for $C_{22}H_{20}N_6Ru_2Cl_2P_2F_{12}$ (931.41): C, 28.37; H, 2.16; N, 9.02. Found: C, 38.21; H, 2.45; N, 8.98%. ^1H NMR (400 MHz, CD_3CN): δ = 9.68 (d, 2H, ^3J = 2.8 Hz), 8.79 (s, 1H), 8.71 (d, 2H, ^3J = 7.2 Hz), 8.32 (s, 1H), 7.01 (dd, 2H, ^3J = 2.0 Hz), 6.15 (s, 12H, C_6H_6);. ESI-MS (*m/z*): 786.1 $[M^{2+}+PF_6^-]^+$, 427.2 $[M-PF_6]^+$; IR (KBr, cm^{-1}): 845s $\nu_{(P-F)}$, 1598m, 1559m, 1521m ($\nu_{C=N}$ L1), 2995m, 3447w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}$ cm^{-1})}: 259(0.21), 318(0.23), 380(0.08).

*2.6.2. [{(η^6-C_6H_6)RuCl}$_2$(L2)]$(PF_6)_2$ ([**14**]$(PF_6)_2$)*

Yield: 71 mg, 74.7%.

Elemental Anal. Calc. for $C_{24}H_{24}N_6Ru_2Cl_2P_2F_{12}$ (959.46): C, 30.04; H, 2.52; N, 8.76. Found: C, 29.95; H, 2.58; N, 8.61%. ^1H NMR (400 MHz, CD_3CN): δ = 9.46 (s, 1H), 8.58 (d, 2H, ^3J = 8.4 Hz), 8.15 (s, 1H), 7.25 (d, 2H, ^3J = 4.6 Hz), 6.24 (s, 12H, C_6H_6), 2.83 (s, 3H,CH_3), 2.81 (s, 3H, CH_3); ESI-MS (*m/z*):814.2 $[M^{2+}+PF_6^-]^+$, 455.2 $[M-PF_6]^+$; IR (KBr, cm^{-1}): 843s $\nu_{(P-F)}$, 1601m, 1557m, 1524m ($\nu_{C=N}$

L2), 3010m, 3449w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}$ cm^{-1})}: 262(0.29), 310(0.75), 374(0.12).

*2.6.3. [{(η^6-C_6H_6)RuCl}$_2$(L3)](PF$_6$)$_2$ ([**15**](PF$_6$)$_2$)*

Yield: 81 mg, 82.6%.

Elemental Anal. Calc. for $C_{24}H_{28}N_6Ru_2Cl_2P_2F_{12}$ (987.52): C, 31.62; H, 2.86; N, 8.51. Found: C, 31.50; H, 2.95; N, 8.33%. ^{1}H NMR (400 MHz, CD_3CN): δ = 10.02 (s, 1H), 7.68 (s, 1H), 6.72 (s, 2H), 6.21 (s, 12H, C_6H_6), 2.81 (s, 6H, CH_3), 2.69 (s, 6H, CH_3); ESI-MS (*m/z*): 842.4 [M^{2+}+PF_6^-]$^+$, 483.3 [M−PF_6]$^+$; IR (KBr, cm^{-1}): 843s $\nu_{(P-F)}$, 1606m, 1560m, 1524m ($\nu_{C=N}$ L3), 3050m, 3451w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}$ cm^{-1})}: 271(0.18), 315(0.81), 380(0.11).

*2.6.4. [{(η^6-*p*-^{i}PrC$_6$H$_4$Me)RuCl}$_2$(L1)](PF$_6$)$_2$ ([**16**](PF$_6$)$_2$)*

Yield: 87 mg, 83.6%.

Elemental Anal. Calc. for $C_{30}H_{36}N_6Ru_2Cl_2P_2F_{12}$ (1043.62): C, 34.53; H, 3.48; N, 8.05. Found: C, 34.42; H, 3.47; N, 7.96%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.65 (d, 2H, ^3J = 2.4 Hz), 8.71 (d, 2H, ^3J = 4.6 Hz), 8.68 (s, 1H), 7.28 (s, 1H), 7.06 (dd, 2H, ^3J = 2.4 Hz), 6.08 (d, 2H, ^3J = 6.4 Hz, Ar_{p-cy}), 6.06 (d, 2H, ^3J = 6.4 Hz, Ar_{p-cy}), 5.99 (d, 2H, ^3J = 6.0 Hz, Ar_{p-cy}), 5.93 (d, 2H, ^3J = 6.0 Hz, Ar_{p-cy}), 2.74–2.69 (sept, 2H, ^3J = 6.2 Hz, $CH(CH_3)_2$), 2.18 (s, 6H, Ar_{p-cy}–Me), 1.14 (d, 6H, ^3J = 6.8 Hz, $CH(CH_3)_2$), 1.04 (d, 6H, ^3J = 7.6 Hz, $CH(CH_3)_2$); ESI-MS (*m/z*): 898.2 [M^{2+}+PF_6^-]$^+$, 483.3 [M−PF_6]$^+$; IR (KBr, cm^{-1}): 844s $\nu_{(P-F)}$, 1599m, 1560m, 1525m ($\nu_{C=N}$ L1), 2995m, 3447w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}$ cm^{-1})}: 260(0.29), 310(0.58), 378(0.13).

*2.6.5. [{(η^6-*p*-^{i}PrC$_6$H$_4$Me)RuCl}$_2$(L2)](PF$_6$)$_2$ ([**17**](PF$_6$)$_2$)*

Yield: 77 mg, 71.9%.

Elemental Anal. Calc. for $C_{32}H_{40}N_6Ru_2Cl_2P_2F_{12}$ (1071.67): C, 35.86; H, 3.76; N, 7.84. Found: C, 43.78; H, 3.94; N, 13.92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.38 (s, 1H), 8.51 (d, 2H, ^3J = 2.8 Hz), 7.89 (s, 1H), 6.75 (d, 2H, ^3J = 9.6 Hz), 6.01 (d, 2H, ^3J = 6.0 Hz, Ar_{p-cy}), 5.99 (d, 2H, ^3J = 6.04 Hz, Ar_{p-cy}), 5.96 (d, 2H, ^3J = 6.0 Hz, Ar_{p-cy}), 5.96 (d, 2H, ^3J = 6.04 Hz, Ar_{p-cy}), 2.81 (s, 6H, CH_3), 2.75 (sept, 2H, $CH(CH_3)_2$), 2.26 (s, 6H, Ar_{p-cy}–Me), 1.19 (d, 6H, ^3J = 3.2 Hz, $CH(CH_3)_2$), 1.17 (d, 6H, ^3J = 3.2 Hz, $CH(CH_3)_2$); ESI-MS (*m/z*): 926.2 [M^{2+}+PF_6^-]$^+$, 513.2 [M−PF_6]$^+$; IR (KBr, cm^{-1}): 843s $\nu_{(P-F)}$, 1601m, 1557m, 1524m ($\nu_{C=N}$ L2), 3011m, 3451w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}$ cm^{-1})}: 271(0.18), 315(0.81), 380(0.11).

*2.6.6. [{(η^6-*p*-^{i}PrC$_6$H$_4$Me)RuCl}$_2$(L3)](PF$_6$)$_2$ ([**18**](PF$_6$)$_2$)*

Yield: 90 mg, 82.5%.

Elemental Anal. Calc. for $C_{34}H_{44}N_6Ru_2Cl_2P_2F_{12}$ (1099.73): C, 37.13; H, 4.03; N, 7.64. Found: C, 37.05; H, 4.07; N, 7.64. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.91 (s, 1H), 7.67 (s, 1H), 6.68 (s, 2H), 6.11 (d, 2H, ^3J = 6.4 Hz, Ar_{p-cy}), 6.08 (d, 2H, ^3J = 6.2 Hz, Ar_{p-cy}), 5.95 (d, 2H, ^3J = 6.0 Hz, Ar_{p-cy}), 5.89 (d, 2H, ^3J = 6.4 Hz, Ar_{p-cy}), 2.80 (s, 6H, CH_3), 2.76 (s, 6H, CH_3), 2.66 (sept, 2H, $CH(CH_3)_2$), 2.28 (s, 6H, Ar_{p-cy}–Me), 1.09 (d, 6H, ^3J = 3.2 Hz, $CH(CH_3)_2$), 1.06 (d, 6H, ^3J = 3.2 Hz, $CH(CH_3)_2$); ESI-MS (*m/z*): 954.73 [M^{2+}+PF_6^-]$^+$, 538.8 [M−PF_6]$^+$; IR (KBr, cm^{-1}): 843s $\nu_{(P-F)}$, 1608m, 1562m, 1524m ($\nu_{C=N}$ L3), 3041m, 3447w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}$ cm^{-1})}: 263(0.29), 310(0.75), 376(0.12).

*2.7. General procedure for the preparation of the dinuclear complexes **19–24***

A mixture of [(Cp*)M(μ-Cl)Cl]$_2$ (M = Rh and Ir) (0.08 mmol), ligand L (L1, L2 and L3) (0.08 mmol) and 2.5 equivalents of NH_4PF_6 in dry methanol (20 ml) was refluxed at 50 °C for 12 h, resulting a orange color precipitation. The precipitate was separated by filtration, washed with cold methanol, diethyl ether and dried *in vacuo*.

2.7.1. [(Cp)RhCl}$_2$(L1)](PF$_6$)$_2$ ([**19**](PF$_6$)$_2$)*

Yield: 66 mg, 79.5%.

Elemental Anal. Calc. for $C_{30}H_{38}N_6Rh_2Cl_2P_2F_{12}$ (1049.31): C, 34.34; H, 3.65; N, 8.01. Found: C, 34.23; H, 3.75; N, 7.91%. ^{1}H NMR (400 MHz, CD_3CN): δ = 9.18 (s, 1H), 8.84 (d, 2H, ^3J = 3.2 Hz), 8.36 (d, 2H, ^3J = 1.6 Hz), 8.01 (s, 1H), 6.92 (dd, 2H, ^3J = 1.6 Hz), 1.81 (s, 30H, C_5Me_5); ESI-MS (*m/z*): 904.3 [M^{2+}+PF_6^-]$^+$, 485.2 [M−PF_6]$^+$; IR (KBr, cm^{-1}): 845s $\nu_{(P-F)}$, 1592m, 1558m, 1522m ($\nu_{C=N}$ L1), 2995m, 3447w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}$ cm^{-1})}: 271(0.18), 315(0.81), 380(0.11).

2.7.2. [(Cp)RhCl}$_2$(L2)](PF$_6$)$_2$ ([**20**](PF$_6$)$_2$)*

Yield: 60 mg, 70.5%.

Elemental Anal. Calc. for $C_{32}H_{42}N_6Rh_2Cl_2P_2F_{12}$ (1077.36): C, 35.67; H, 3.93; N, 7.80. Found: C, 35.26; H, 3.99; N, 7.61%. ^{1}H NMR (400 MHz, CD_3CN): δ = 9.05 (s, 1H), 8.46 (d, 2H, ^3J = 6.0 Hz), 8.12 (s, 1H), 6.79 (d, 2H, ^3J = 4.6 Hz), 2.76 (s, 3H, CH_3), 2.73 (s, 3H, CH_3), 1.77 (s, 30H, C_5Me_5); ESI-MS (*m/z*):513.8 [M−PF_6], 932.1 [M^{2+}+PF_6^-]$^+$, 513.8 [M−PF_6]$^+$; IR (KBr, cm^{-1}): 845s $\nu_{(P-F)}$, 1598m, 1559m, 1521m ($\nu_{C=N}$ L2), 2998m, 3449w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}$ cm^{-1})}: 259(0.11), 315(0.51), 380(0.08).

2.7.3. [(Cp)RhCl}$_2$(L3)](PF$_6$)$_2$ ([**21**](PF$_6$)$_2$)*

Yield: 67 mg, 77.1%.

Elemental Anal. Calc. for $C_{34}H_{46}N_6Rh_2Cl_2P_2F_{12}$ (1105.41): C, 36.94; H, 4.19; N, 7.60. Found: C, 36.86; H, 4.15; N, 7.58%. ^{1}H NMR (400 MHz, CD_3CN): δ = 9.09 (s, 1H), 7.36 (s, 1H), 6.79 (s, 2H), 2.84 (s, 6H, CH_3), 2.79 (s, 6H, CH_3), 1.88 (s, 30H, C_5Me_5); ESI-MS (*m/z*): 960.2 [M^{2+}+PF_6^-]$^+$, 541.81 [M−PF_6]$^+$; IR (KBr, cm^{-1}): 843s $\nu_{(P-F)}$, 1601m, 1557m, 1524m ($\nu_{C=N}$ L3), 3010m, 3442w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}$ cm^{-1})}: 269(0.18), 315(0.48), 371(0.10).

2.7.4. [(Cp)IrCl}$_2$(L1)](PF$_6$)$_2$ ([**22**](PF$_6$)$_2$)*

Yield: 72 mg, 75.7%.

Elemental Anal. Calc. for $C_{30}H_{38}N_6Ir_2Cl_2P_2F_{12}$ (1227.93): C, 29.34; H, 3.12; N, 6.84. Found: C, 29.23; H, 3.15; N, 6.71%. ^{1}H NMR (400 MHz, CD_3CN): δ = 9.01 (s, 1H), 8.84 (d, 2H, ^3J = 3.2 Hz), 8.41 (d, 2H, ^3J = 2.4 Hz), 8.03 (s, 1H), 6.95 (dd, 2H, ^3J = 1.6 Hz), 1.79 (s, 30H, C_5Me_5); ESI-MS (*m/z*): 1082.2 [M^{2+}+PF_6^-]$^+$, 575.2 [M−PF_6]$^+$; IR (KBr, cm^{-1}): 845s $\nu_{(P-F)}$, 1598m, 1559m, 1521m ($\nu_{C=N}$ L1), 2995m, 3447w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}$ cm^{-1})}: 260(0.19), 310(0.67), 368(0.11).

2.7.5. [(Cp)IrCl}$_2$(L2)](PF$_6$)$_2$ ([**23**](PF$_6$)$_2$)*

Yield: 60 mg, 61%.

Elemental Anal. Calc. for $C_{32}H_{42}N_6Ir_2Cl_2P_2F_{12}$ (1255.98): C, 30.60; H, 3.37; N, 6.69. Found: C, 30.45; H, 3.48; N, 6.51%. ^{1}H NMR (400 MHz, CD_3CN): δ = 9.01 (s, 1H), 8.48 (d, 2H, ^3J = 6.4 Hz), 8.15 (s, 1H), 6.71 (d, 2H, ^3J = 4.6 Hz), 2.63 (s, 6H, CH_3), 1.75 (s, 30H, C_5Me_5); ESI-MS (*m/z*):1111.1 [M^{2+}+PF_6^-]$^+$, 603.1 [M−PF_6]$^+$; IR (KBr, cm^{-1}): 844s $\nu_{(P-F)}$, 1599m, 1560m, 1525m ($\nu_{C=N}$ L2), 3002m, 3441w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}$ cm^{-1})}: 265(0.16), 315(0.56), 371(0.09).

2.7.6. [(Cp)IrCl}$_2$(L3)](PF$_6$)$_2$ ([**24**](PF$_6$)$_2$)*

Yield: 74 mg, 74%.

Elemental Anal. Calc. for $C_{34}H_{46}N_6Ir_2Cl_2P_2F_{12}$ (1284.04): C, 31.80; H, 3.61; N, 6.54. Found: C, 31.76; H, 3.78; N, 6.33%. ^{1}H NMR (400 MHz, CD_3CN): δ = 9.04 (s, 1H), 7.31 (s, 1H), 6.68 (s, 2H), 2.83 (s, 6H, CH_3), 2.79 (s, 6H, CH_3), 1.82 (s, 30H, C_5Me_5); ESI-MS (*m/z*): 1139.5 [M^{2+}+PF_6^-]$^+$, 631.2 [M−PF_6]$^+$; IR (KBr, cm^{-1}): 843s $\nu_{(P-F)}$, 1608m, 1562m, 1524m ($\nu_{C=N}$ L3), 3016m, 3450w; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}$ cm^{-1})}: 268(0.19), 321(0.61), 376(0.13).

3. Results and discussion

3.1. Syntheses of ligands and complexes

Ligands L2 and L3 were prepared from the corresponding pyrazolato anion and 4,6-dichloropyrimidine. Reaction of half equivalent of dinuclear arene ruthenium complexes $[(\eta^6\text{-arene})Ru(\mu\text{-Cl})Cl]_2$ (arene = C_6H_6, *p*-$^{i}PrC_6H_4Me$) with one equivalent of 4,6-disubstituted pyrimidine ligands *viz.* 4,6-bis(pyrazolyl)pyrimidine (L1), 4,6-bis(3-methyl-pyrazolyl)pyrimidine (L2) or 4,6-bis(3,5-dimethyl-pyrazolyl)pyrimidine (L3) in methanol generates the mononuclear complexes $[(\eta^6\text{-}C_6H_6)Ru(L)Cl]^+$ (L = L1, **1**; L2, **2**; L3, **3**), $[(\eta^6\text{-}p\text{-}^{i}PrC_6H_4Me)Ru(L)Cl]^+$ (L = L1, **4**; L2, **5**; L3, **6**), respectively (Scheme 2). The homologous complexes with two coordinated arene ruthenium fragments, $[\{(\eta^6\text{-}C_6H_6)RuCl\}_2(L)](PF_6)_2$ (L = L1, **13**; L2, **14**; L3, **15**) and $[\{(\eta^6\text{-}p\text{-}^{i}PrC_6H_4Me)RuCl\}_2(L)](PF_6)_2$ (L = L1, **16**; L2, **17**; L3, **18**), were prepared when a 1:1 M ratio was used and over prolonged reaction times (Scheme 2). All these cationic ruthenium complexes were isolated as their hexafluorophosphate salts.

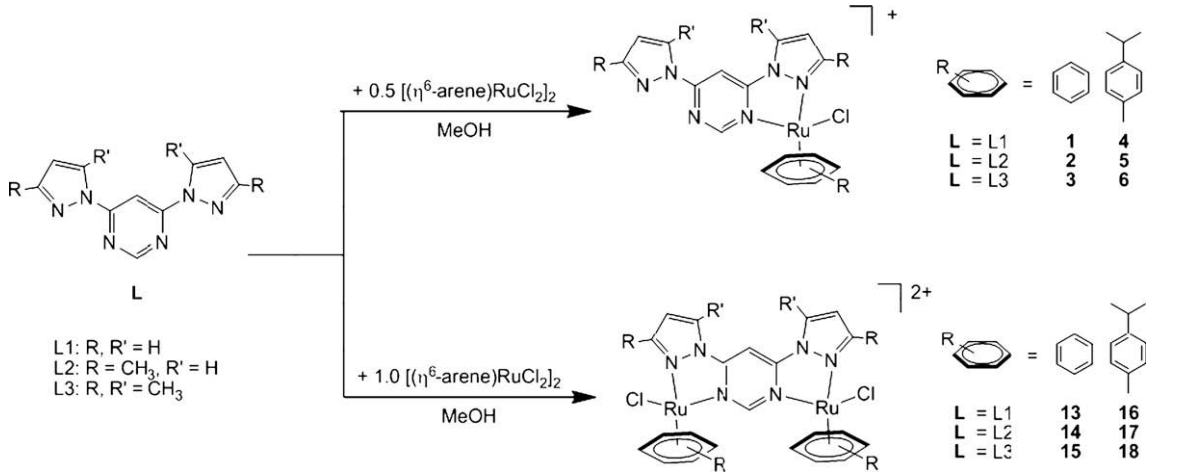
Similarly, the reaction of half equivalent of the dimeric chloro-bridged complexes $[(Cp^*)M(\mu\text{-Cl})Cl]_2$ (M = Rh, Ir) with 4,6-disubstituted-pyrimidine ligands (L) in methanol generates the mononuclear cationic complexes of the type $[(Cp^*)Rh(L)Cl]^+$ (L = L1, **7**; L2, **8**; L3, **9**), $[(Cp^*)Ir(L)Cl]^+$ (L = L1, **10**; L2, **11**; L3, **12**), respectively (Scheme 3). The homologous complexes with two coordinated Cp*Rh or Cp*Ir fragments, $[\{(Cp^*)RhCl\}_2(L)](PF_6)_2$ (L = L1, **19**; L2, **20**; L3, **21**) and $[\{(Cp^*)IrCl\}_2(L)](PF_6)_2$ (L = L1, **22**; L2, **23**; L3, **24**), were prepared when a 1:1 M ratio was used and at prolonged reaction times (Scheme 3). All these cationic rhodium or iridium complexes were isolated as their hexafluorophosphate salts.

When the mononuclear complexes [**1**]PF_6 – [**12**]PF_6 were further reacted with half mole of arene ruthenium or Cp*Rh or Ir dimers in acetonitrile solution, no reaction took place and isolated as starting compounds. Also attempts to synthesize hetero-nuclear complexes by reaction of the mononuclear complexes with other metal atoms led to no reaction.

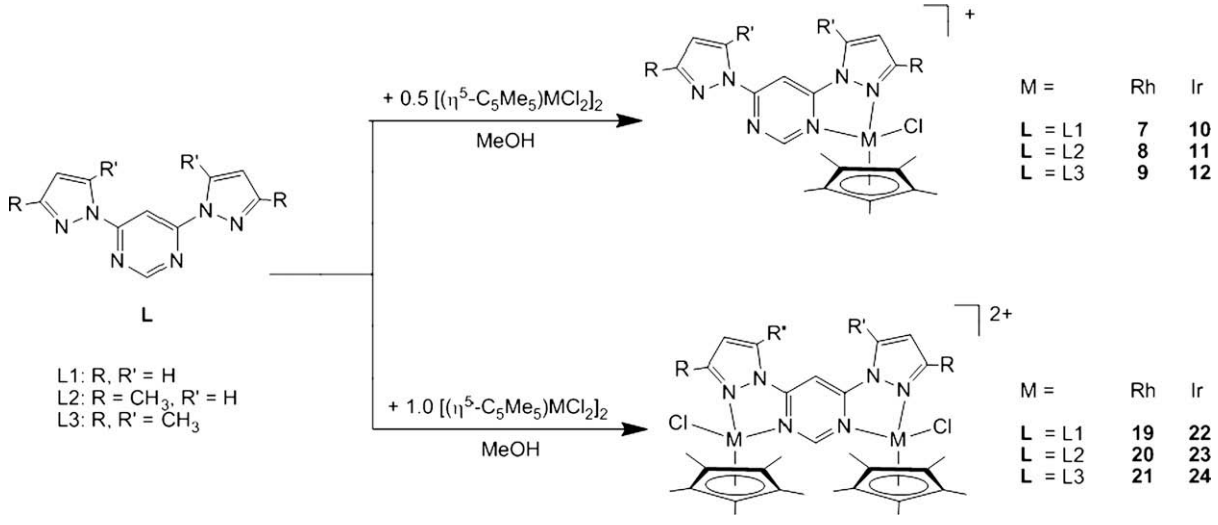
All these complexes are orange yellow in color, non-hygroscopic, air stable solids. They are soluble in acetonitrile but partially soluble in dichloromethane, chloroform and acetone.

3.2. Characterization of mononuclear complexes *1* – *12*

All these mononuclear complexes were characterized by IR, ^1H NMR, mass and elemental analysis. The infrared spectra of the complexes [**1**]PF_6 – [**12**]PF_6 exhibit a strong band in the region



Scheme 2.



Scheme 3.

844–850 cm^{-1}, a typical ν_{P-F} stretching band for the PF_6 anions. Moreover, all complexes show absorption bands around 1600–1610 cm^{-1}, 1550–1558 cm^{-1} and 1522–1528 cm^{-1} corresponding to $\nu_{C=N}$ vibrations of pyrazole and pyrimidine moieties [52] besides these absorptions 2990–3050 and 3400–3450 were observed.

The mass spectra of these complexes exhibited, as expected, the corresponding molecular ion peaks *m/z* at 427, 455, 483, 483, 511, 538, 485, 513, 541, 575, 603 and 631. For instance complex [**1**]PF_6 shown four fragments, a molecular ion peak at 427 $[M]^+$, 391 $[M-Cl]^+$, 313 [M−Cl-arene]$^+$ and 213 [L+1].

The ^1H NMR spectra of the free ligands L1–L3 exhibit a characteristic set of five resonances for the eight protons of pyrazole and pyrimidine rings, since the pyrazole rings are in symmetrical position. Upon coordination with the metal atom, each mononuclear complex has shown seven to eight set of resonances for the ligand L1–L3 protons in the region δ = 9.56–6.78, δ = 9.41–2.43, and δ = 9.34–2.17, respectively. It indicates the formation of mononuclear complexes. The resonances of the coordinated pyrazole and pyrimidine rings protons shifted to higher frequency as a consequence of their coordination to the ruthenium or rhodium or iridium atom. However, arene ruthenium complexes [**1**]PF_6 – [**6**]PF_6, the resonances of ligand protons significantly shifted to down field compared to Cp*Rh or Cp*Ir complexes, [**7**]PF_6 – [**12**]PF_6. Besides these ligand resonances, complexes [**1**]PF_6 – [**3**]PF_6 exhibit a singlet for the benzene ring protons at δ = 6.20–5.93, complexes [**4**]PF_6 to [**6**]PF_6 exhibit a septet at δ = 2.70 for the protons of the isopropyl group and a singlet at δ = 2.17 for the methyl protons of the *p*-cymene ring. The ring protons and methyl protons of the isopropyl group of the *p*-cymene ligand have shown an unusual pattern of resonances. For instance, the methyl protons of the isopropyl group displays two doublets at *ca.* δ = 1.18–1.07, instead of one doublet as in the starting complex. The aromatic protons of the *p*-cymene ligand display four doublets, instead of two doublets as in the starting precursor. This unusual pattern is due 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 [53,54]. Complexes [**1**]PF_6 to [**12**]PF_6 exhibit a singlet at δ = 1.71–1.55 for the five methyl groups of the Cp* ligand. The chemical shift of the co-ligands arene or Cp* ring protons are shifted to down field compared to the starting precursors.

3.3. Molecular structure of selected mononuclear complexes

The molecular structure of the [(η^6-C_6H_6)Ru(L3)Cl]PF_6 ([**3**]PF_6), [(η^6-*p*-^{i}PrC_6H_4Me)Ru(L3)Cl]PF_6 ([**6**]PF_6) as well as the Cp* rhodium complex [(Cp*)Rh(L1)Cl]PF_6 ([**7**]PF_6) have been established by single crystal X-ray structure analysis. These cationic complexes show a typical piano-stool geometry with the metal center being coordinated by an aromatic ligand, a terminal chloro ligand and a chelating 4,6-disubstituted-pyrimidine ligand. The metal atom possesses an octahedral arrangement with two *cis*-nitrogen atoms of the pyrazolyl-pyrimidine ligand acting as a bidentate chelating ligand in a five-membered ring chelating fashion involving one nitrogen atom of the pyrazolyl moiety and the nitrogen atom of the pyrimidine group. The structures are shown in Figs. 1–3. Selected bond lengths and angles for [**3**]PF_6, [**6**]PF_6 and [**7**]PF_6 are presented in Table 2.

In the mononuclear complexes [**3**]PF_6 and [**7**]PF_6 the N1-metal distance (2.076 and 2.106 Å) of the pyrazolyl moiety is slightly shorter than the corresponding pyrimidinyl, N3-metal distance (2.092, and 2.138 Å), in contrast to complex [**6**]PF_6 in which the N1-metal (2.102 Å) distance is slightly longer than the corresponding N3-metal distance (2.093(2) Å). The Rh–N bond distance (2.106(3) and 2.138(3) Å) in **7** is slightly longer than the corresponding distances of ruthenium complex **3** (2.076(3) and 2.092(2) Å) and complex **6** (2.102 and 2.093), while the M−Cl

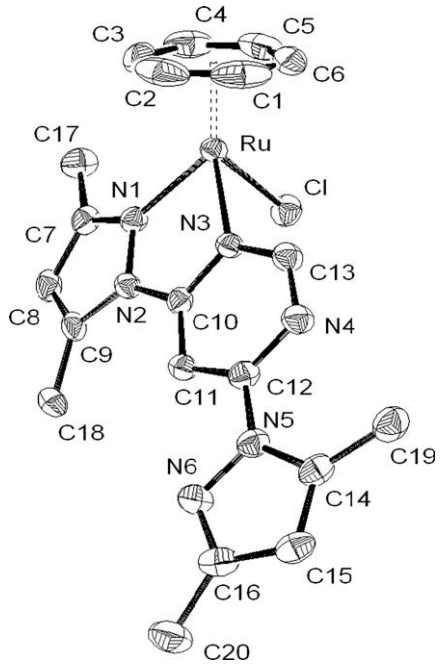


Fig. 1. Molecular structure of [**3**]$PF_6 \cdot H_2O$ at 50% probability level. Hydrogen atoms, water molecule and hexafluorophosphate anion have been omitted for clarity.

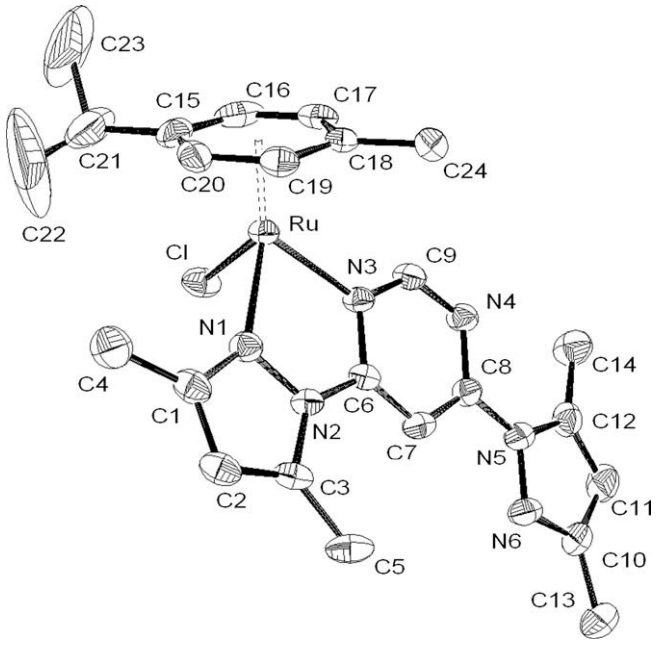


Fig. 2. Molecular structure of [**6**]PF_6 at 50% probability level. Hydrogen atoms and hexafluorophosphate anion have been omitted for clarity.

[2.402(7), 2.388(8) and 2.400(6)] bond lengths show no significant differences in all the cations and similar reported values [55,56]. The N–M–N bond angles [75.33(7) in **3** and 75.56°(9) in **6**] are similar to that of complexes [(η^6*p*-^{i}PrC_6H_4Me)RuCl(2,3-bis(α-pyridyl)quinoxaline)]$^+$ [76.2 (2)°] [57]. The distances between the ruthenium atom and the centroid of the C_6 aromatic ring in **3** and **6** are comparable (1.69 and 1.68 Å) but quite shorter than the distance between the rhodium atom and the C_5 aromatic ring observed in **7** (1.77 Å). The M–N1 bond distances [2.076(9) to 2.102(2) Å] are comparable to those in g_6-p-^{i}PrC_6H_4Me

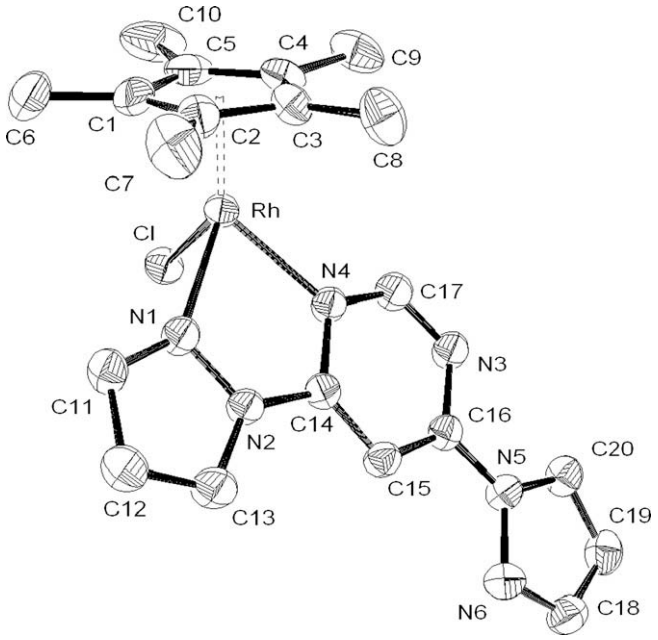


Fig. 3. Molecular structure of [**7**]PF_6 at 50% probability level. Hydrogen atoms and anion have been omitted for clarity.

$[(\eta^6\text{-}C_6H_6)RuCl(2\text{-}(1\text{-imidazol-2-yl})pyridine)]^+$ [58] and $[(Cp^*)Ir(2\text{-}(2'\text{-pyridyl})\text{-imidazole})Cl]^+$ [59].

As amplified in Figs. 1–3, all cations possess metal-centered chirality as the metal atom is coordinated to four different ligator atoms. However, since none of the ligands contain chiral centers, they are all obtained as a racemic mixture and they all crystallize in the centrosymmetric space group $P\bar{1}$.

In the crystal packing of [**3**]$PF_6{\cdot}H_2O$, the hexafluorophosphate anion sits on side of the cationic complex and interacts with an hydrogen atom of the C_6H_6 ligand (see supplementary material). The hexafluorophosphate anion interacts with C_6H_6 ligand through C–H···F contacts: the C···F distances being 3.22 and 3.26 Å with C–H···F angles of 148.9 and 138.3°, respectively. In addition to this the oxygen atom interacts with one of the hydrogen atoms of ligand L1through C–H···O contact: the C···O distance being 3.10 Å and C–H···O angle is 149.06°.

3.4. Characterization of the dinuclear complexes

The infrared spectra of the dinuclear complexes [**13**]$(PF_6)_2$ – [**24**]$(PF_6)_2$ exhibit a similar trend as for the mononuclear complexes [**1**]PF_6 – [**12**]PF_6. The mass spectra of these complexes exhibited two main peaks; a minor peak with an approximately 50% intensity attributed to $[M{-}PF_6]^+$ at *m/z* 786, 814, 842, 898, 926, 954, 904, 932, 960, 1082, 1110 and 1138, respectively, and a major peak which corresponds to the loss of an $[(arene/Cp^*)MCl]^+$ fragment, thus giving the corresponding mononuclear cations $[\mathbf{1}{-}PF_6]^+$ – $[\mathbf{12}{-}PF_6]^+$ at *m/z* = 427, 455, 483, 483, 511, 538, 485, 513, 541, 575, 603 and 631.

The ^1H NMR spectra of the dinuclear complexes [**13**]$(PF_6)_2$ – [**24**]$(PF_6)_2$, exhibit five distinct resonances, which are assigned to pyrazole or substituted pyrazoles and pyrimidine ring protons of the ligand L1 or L2 or L3, indicating the formation of dinuclear complexes. The number of distinct resonances of these complexes is similar to the number of distinct resonances of free ligands, indicating that the pyrazole rings of the ligands remain symmetrical even after formation of the complexes. These results indicate the formation of dinuclear complexes. The resonances of the coordinated pyrazole and pyrimidine protons shifted to considerable down filed as compared to mononuclear complexes, a consequence of their coordination to two ruthenium, rhodium or iridium atoms. However, in the arene ruthenium complexes [**13**]$(PF_6)_2$ – [**18**]$(PF_6)_2$, the resonances of the ligand protons significantly shifted to down field compared to Cp*Rh or Ir complexes, [**19**]$(PF_6)_2$ – [**24**]$(PF_6)_2$. Besides these resonances complexes

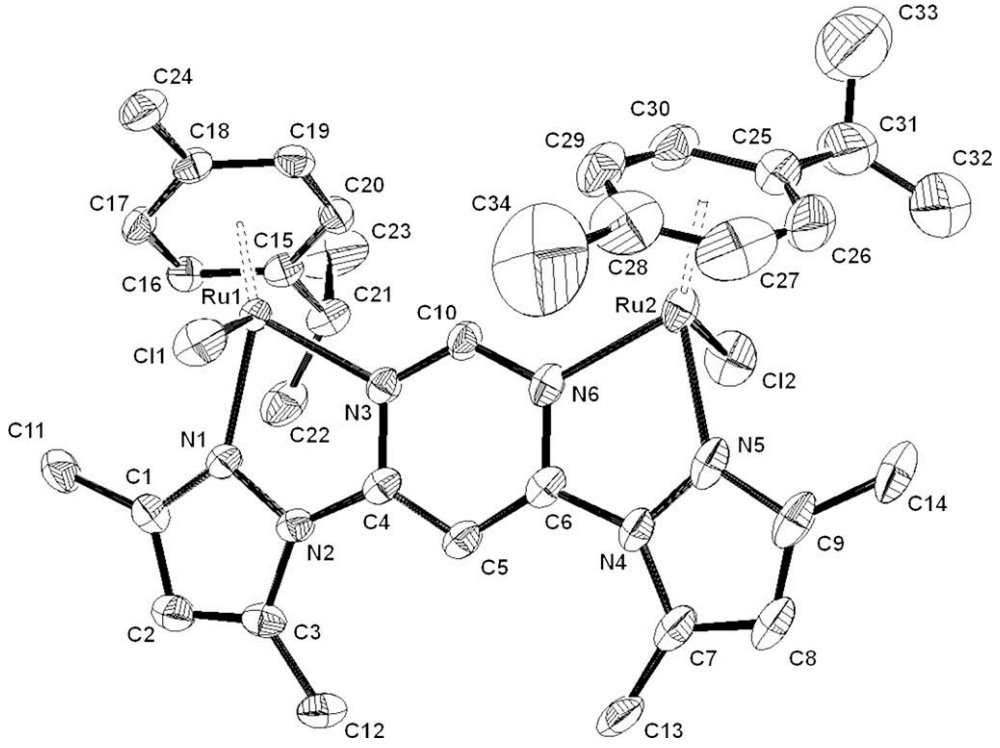


Fig. 4. Molecular structure of [**18**]$(PF_6)_2{\cdot}H_2O$ at 50% probability level. Hydrogen atoms, water molecule and hexafluorophosphate anions have been omitted for clarity.

[**13**]$(PF_6)_2$ – [**15**]$(PF_6)_2$ exhibit a singlet for both benzene ring protons at δ = 6.24 and 6.15 ppm, complexes [**16**]$(PF_6)_2$ – [**18**]$(PF_6)_2$ exhibit a similar trend like the mononuclear complexes [**4**]PF_6 – [**4**]PF_6. A septet at δ = 2.70 for the protons of the isopropyl group, a singlet at δ = 2.17 for the methyl protons of *p*-cymene ring, four doublets *ca.* δ = 6.09–5.93 for the ring protons of the *p*-cymene ligand and finally methyl protons of the isopropyl group displays two doublets at *ca.* δ = 1.18 and 1.07. Complexes [**19**]$(PF_6)_2$ – [**24**]$(PF_6)_2$ exhibit a singlet in the region δ = 1.88–1.77 for the five methyl groups of the Cp* ligand. The chemical shift of the arene co-ligands or Cp* ring protons are shifted to higher frequency compared to the starting precursors as well as compared to the mononuclear complexes.

*3.5. Molecular structure of the dinuclear complex [**18**](PF$_6$)$_2$*

The molecular structure of $[\{(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)RuCl\}_2(L3)]^{2+}$ ([**18**]$(PF_6)_2$) has been established by single crystal X-ray structure analysis. Selected bond lengths and angles are presented in Table 2. The dinuclear complex [**18**]$(PF_6)_2$ shows a typical piano-stool geometry for the ruthenium atoms with the metal centers being coordinated by the aromatic ligand, a terminal chloride and a chelating *N,N*-ligand (Fig. 4). The compound [**18**]$(PF_6)_2$ contains two Ru(II) metal centers which are bonded to a η^6-*p*-$Pr^iC_6H_4Me$ ligand and bridged by the L3 ligand through its nitrogen atoms. Interestingly, the dinuclear complex [**18**]$(PF_6)_2$ reveals a *trans* conformation of the two chloro ligands (Fig. 4). The distance between the ruthenium atoms and the corresponding centroid of the η^6-*p*-$^iPrC_6H_4Me$ ring is 1.68 and 1.67 Å. These distances are comparable to those in the related complex cation $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru$(2-acetylthiazoleazine)Cl$]^+$ [60].

The Ru–N bond distances ranging from 2.072(3) to 2.092(3) Å are shorter than in the mononuclear complex [**6**]PF_6 [2.102(3) and 2.093(3) Å], interestingly the Ru to N1 or N5 (pyrazole) distances are shorter than the Ru–N3 or N6 (pyrimidine) distances in the dinuclear complex [**18**]$(PF_6)_2$, where as it is opposite in mononuclear complex [**6**]PF_6, while the ruthenium–chlorine bond distances are comparable. In complex [**18**]$(PF_6)_2$, the isopropyl group of the *p*-cymene ligand at Ru1 center located opposite to the halide ligand in order to reduce steric interactions, while at Ru2 the isopropyl group is located on same side to the halide ligand.

Complex [**18**]$(PF_6)_2$ crystallizes with one molecule of water per asymmetric unit, forming an hydrogen-bonded network to the chloride atom and the fluorine atom of the hexafluorophosphate anion (Fig. 5). The water molecule interacts with chloride ligand through O–H···Cl contacts: the O···Cl distance being 3.26 Å with an O–H···Cl angle of 156.3°. In addition to this, the water molecule interacts with one of the fluoride atoms of the hexafluorophosphate anion through F···H–O contacts: the F···O distance being 3.51 Å and the F···H–O angle 154.09°.

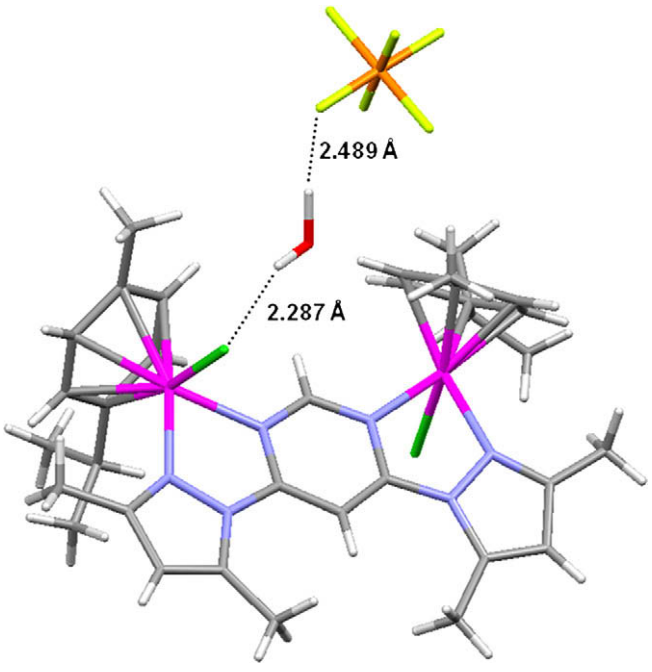


Fig. 5. Hydrogen bond network in [**18**]$(PF_6)_2{\cdot}H_2O$ showing the intermolecular interactions involving an hexafluorophosphate anion, a water molecule and cation $[\mathbf{18}]^+$.

4. UV–Vis spectroscopy

Electronic absorption spectra of the mononuclear complexes [**1**]PF_6 – [**12**]PF_6 as well as the dinuclear complexes [**13**]$(PF_6)_2$ – [**24**]$(PF_6)_2$ were acquired in acetonitrile, at 10^{-5} M concentration in the range 250–550 nm. Electronic spectra of representative complexes are depicted in Fig. 6. The 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) $d\pi(M) \rightarrow \pi^*$ (L1 – ligand) bands in the visible region [61]. Since the low spin d^6 configuration of the mononuclear complexes provides filled orbitals of suitable symmetry at the Ru(II), Rh(III) and Ir(III) centers, these can interact with low lying π^* orbitals of the ligands. All these mononuclear complexes [**1**]PF_6 – [**12**]PF_6 show two medium intensity bands in the region 261–310 nm, an intense band in the region 340–380 nm in UV region and a low energy absorption band in the visible region 450–470 nm. Where as the dinuclear complexes [**13**]$(PF_6)_2$ – [**24**]$(PF_6)_2$ shown similar number of bands in higher frequency region, for instance a medium intensity band in the region 260–275 nm, a high intensity band in the region 318–322 nm and a broad band in the region 356–418 nm. The medium intensity bands in UV region is assigned to π–π^*, a high intensity band in UV region is assigned to inter and intra-ligand π–π^*/n – π^* transitions [62,63], while the low energy absorption band in the visible region is assigned to metal-to-ligand charge transfer (MLCT) (t_{2g}–π^*).

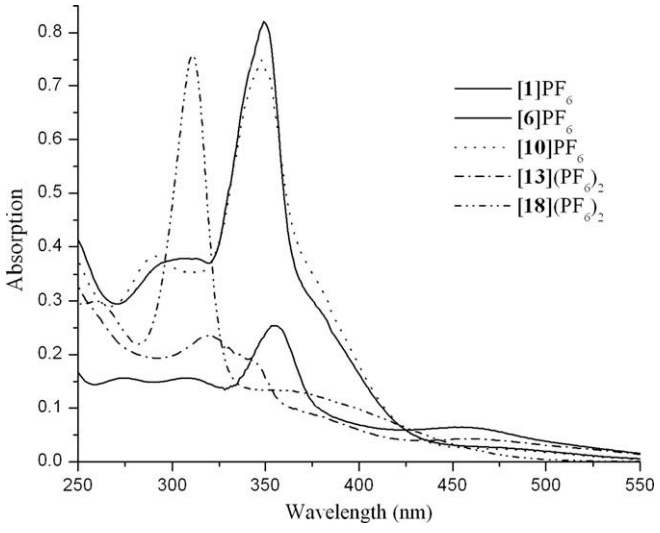


Fig. 6. UV–Vis electronic spectra of selected complexes in acetonitrile at 298 K.

5. Conclusions

We have described and characterized new mono and dinuclear ruthenium, rhodium and iridium complexes with the ligands L1, L2 and L3, in good yield, which are remarkably stable in air as well as in solution. In both, mono and dinuclear complexes, the metal atom are bonded with the N-atom of the pyrazole moiety and the N-atom of the pyrimidine moiety. But our effort to make hetero-nuclear complexes by using second binding site of the mononuclear complexes was unsuccessful, since coordination of the first metallic center does not induce the bonding in the second position in a kind of chemical symbiosis driven by the ligand or the metal center.

Acknowledgement

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Appendix A. Supplementary material

CCDC 742491, 742492, 742493 and 751116 contain the supplementary crystallographic data for **3**, **6**, **7** and **18**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.11.030.

References

[1] S. Trofimenko, Chem. Rev. 93 (1993) 943.
[2] M.D. Ward, Rep. Prog. Chem., Sect. A: Inorg. Chem. 91 (1994) 317.
[3] A. Juris, S. Barigelletti, S. Campagna, V. Balzani, P. Belser, A. von Zelewsky, Coord. Chem. Rev. (1988) 27.
[4] J.A. Bailey, M.G. Hill, R.E. Marsh, V.M. Miskowski, W.P. Schaefer, H.B. Gray, Inorg. Chem. 34 (1995) 4591.
[5] M.G. Hill, J.A. Bailey, V.M. Miskowski, H.B. Gray, Inorg. Chem. 35 (1996) 4585.
[6] P.-I. Kvam, M.V. Puzyk, V.S. Cotlyr, J. Songstad, K.P. Balashev, Acta Chem. Scand. 50 (1996) 6.
[7] E.W. Abel, A. Gelling, K.G. Orrell, A.G. Osborne, V. Sÿik, Chem. Commun. (1996) 2329.
[8] E.W. Abel, K.G. Orrell, A.G. Osborne, H.M. Pain, V. Sÿik, M.B. Hursthouse, K.M.A. Malik, Chem. Commun. (1996) 253.
[9] M. Akiba, Y. Sasaki, Inorg. Chem. Commun. 1 (1998) 61.
[10] A. Gelling, K.G. Orrell, A.G. Osborne, V. Sÿik, J. Chem. Soc., Dalton Trans. (1998) 937.
[11] M. Navarro, W.F.D. Giovani, J.R. Romero, Synth. Commun. 20 (1990) 399.
[12] N. Grover, H.H. Thorp, J. Am. Chem. Soc. 113 (1991) 7030.
[13] X. Hua, M. Shang, A.G. Lappin, Inorg. Chem. 36 (1997) 3735.
[14] C.M. Che, C. Ho, T.C. Lau, J. Chem. Soc., Dalton Trans. (1991) 901.
[15] S.J. Raven, T.J. Meyer, Inorg. Chem. 27 (1988) 4478.
[16] C.M. Che, W.T. Tang, W.O. Lee, K.Y. Wong, T.C. Lau, J. Chem. Soc., Dalton Trans. (1992) 1551.
[17] A. Dovletoglou, S.A. Adeyemi, M.N. Lynn, D.J. Hodgson, T.J. Meyer, J. Am. Chem. Soc. 112 (1990) 8989.
[18] C.M. Che, V.W.W. Yam, Adv. Inorg. Chem. 39 (1992) 233.
[19] R.A. Binstead, M.E. Mc Guire, A. Dovletoglou, W.K. Seok, L.E. Roecker, T.J. Meyer, J. Am. Chem. Soc. 114 (1992) 173.
[20] A.W. Stumpf, E. Saive, A. Demonceau, A.F. Noels, J. Chem. Soc., Chem. Commun. (1995) 1127.
[21] O. Zava, S.M. Zakeeruddin, C. Danelon, H. Vogel, M. Grätzel, P.J. Dyson, ChemBioChem 10 (2009) 1796.
[22] P.C.A. Bruijnincx, P.J. Sadler, Adv. Inorg. Chem. 61 (2009) 1.
[23] F. Schmitt, P. Govindaswamy, O. Zava, G. Süss-Fink, L. Juillerat-Jeanneret, B. Therrien, J. Biol. Inorg. Chem. 14 (2009) 101.
[24] B. Therrien, G. Süss-Fink, P. Govindaswamy, A.K. Renfrew, P.J. Dyson, Angew. Chem., Int. Ed. 47 (2008) 3773.
[25] P. Govender, N.C. Antonels, J. Mattsson, A.K. Renfrew, P.J. Dyson, J.R. Moss, B. Therrien, G.S. Smith, J. Organomet. Chem. 694 (2009) 3470.
[26] N.P.E. Barry, N.H. Abd Karim, R. Vilar, B. Therrien, Dalton Trans. (2009), doi:10.1039/b913642h.
[27] L. Rigamonti, F. Demartin, A. Forni, S. Righetto, A. Pasini, Inorg. Chem. 45 (2006) 10976.
[28] J. Gradinaru, A. Forni, V. Druta, F. Tessore, S. Zecchin, S. Quici, N. Garbalau, Inorg. Chem. 46 (2007) 884.
[29] G. Gupta, K.T. Prasad, B. Das, G.L.P. Yap, K. Mohan Rao, J. Organomet. Chem. 694 (2009) 2618.
[30] L. Soriano, F.A. Jalón, B.R. Manzano, M. Maestro, Inorg. Chim. Acta 362 (2009) 4486.
[31] K. Sarjit Singh, Y.A. Mozharivskyj, K. Mohan Rao, Z. Anorg. Allg. Chem. 632 (2005) 172.
[32] K. Sarjit Singh, Y.A. Mozharivskyj, C. Thöne, K. Mohan Rao, J. Organomet. Chem. 690 (2005) 3720.
[33] G. Gupta, G.P.A. Yap, B. Therrien, K. Mohan Rao, Polyhedron 28 (2009) 844.
[34] P. Govindaswamy, Y.A. Mozharivskyj, K. Mohan Rao, J. Organomet. Chem. 689 (2004) 3265.
[35] P. Govindaswamy, P.J. Carroll, Y.A. Mozharivskyj, K. Mohan Rao, J. Organomet. Chem. 690 (2005) 885.
[36] P. Govindaswamy, Y.A. Mozharivskyj, K. Mohan Rao, Polyhedron 23 (2004) 3115.
[37] J.K. Hurst, Coord. Chem. Rev. 249 (2005) 313.
[38] C. Sens, I. Romero, M. Rodriguez, A. Llobet, T. Parella, J.B. Buchholz, J. Am. Chem. Soc. 126 (2004) 7798.
[39] I. Romero, M. Rodriguez, C. Sens, J. Mola, Inorg. Chem. 47 (2008) 1824–1834.
[40] M.A. Bennett, T.N. Huang, T.W. Matheson, A.K. Smith, Inorg. Synth. 21 (1982) 74.
[41] M.A. Bennett, T.W. Matheson, G.B. Robertson, A.K. Smith, P.A. Tucker, Inorg. Chem. 19 (1980) 1014.
[42] M.A. Bennett, A.K. Smith, J. Chem. Soc., Dalton Trans. (1974) 233.
[43] J.W. Kang, K. Moseley, P.M. Maitlis, J. Am. Chem. Soc. 91 (1969) 5970.
[44] R.G. Ball, W.A.G. Graham, D.M. Heinekey, J.K. Hoyano, A.D. McMaster, B.M. Mattson, S.T. Michel, Inorg. Chem. 29 (1990) 2023.
[45] C. White, A. Yates, P.M. Maitlis, Inorg. Synth. 29 (1992) 228.
[46] M. Ikeda, K. Maruyama, Y. Nobuhara, T. Yamada, S. Okabe, Chem. Pharm. Bull. 45 (1997) 549.
[47] R. Uson, L.A. Oro, M. Esteban, Polyhedron 3 (1984) 213.
[48] G.M. Sheldrick, Acta Crystallogr., Sect. A46 (1990) 467.
[49] G.M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen, Germany, 1999.
[50] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
[51] I.J. Bruno, J.C. Cole, P.R. Edgington, M. Kessler, C.F. Macrae, P. McCabe, J. Pearson, R. Taylor, Acta Crystallogr., Sect. B58 (2002) 389.
[52] H. van der Poel, G. van Koten, K. Vrieze, Inorg. Chem. 19 (1980) 1145.
[53] P. Govindaswamy, B. Therrien, G. Süss-Fink, P. Štěpnička, Ludvík, J. Organomet. Chem. 692 (2007) 1661.
[54] K.T. Prasad, B. Therrien, K.M. Rao, J. Organomet. Chem. 693 (2008) 3049.
[55] K.T. Prasad, B. Therrien, K.M. Rao, J. Organomet. Chem. (2009), doi:10.1016/j.jorganchem.2009.10.007.
[56] B. Therrien, C. Sa-Mohamed, G. Süss-Fink, Inorg. Chim. Acta 361 (2008) 2601.
[57] R. Lalrempuia, K. Mohan Rao, Polyhedron 22 (2003) 3155.
[58] H. Mishra, R. Mukherjee, J. Orgnomet. Chem. 691 (2006) 3545.
[59] K. Pachhunga, B. Therrien, K.A. Kreisel, G.P.A. Yap, M.R. Kollipara, Polyhedron 26 (2007) 3638.
[60] K.T. Prasad, G. Gupta, A.V. Rao, B. Das, K.M. Rao, Polyhedron 28 (2009) 2649.
[61] E. Binamira-Soriaga, N.L. Keder, W.C. Kaska, Inorg. Chem. 29 (1990) 3167.
[62] C.S. Araújo, M.G.B. Drew, V. Félix, L. Jack, J. Madureira, M. Newell, S. Roche, T.M. Santos, J.A. Thomas, L. Yellowlees, Inorg. Chem. 41 (2002) 2250.
[63] H. Deng, J. Li, K.C. Zheng, Y. Yang, H. Chao, L.N. Ji, Inorg. Chim. Acta 358 (2005) 3430.