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Study of half-sandwich mono and dinuclear complexes of platinum group metals containing pyrazolyl pyridine analogues: Synthesis and spectral characterization

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Abstract. The chelating ligands 3-chloro-6-(3-pyridyl-1-pyrazolyl)pyridazine (*pp-Cl*) and 3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine (*bppp*), were prepared by the condensation of pyridylpyrazole and 3,6-dichloropyridazine. The mononuclear complexes $[(\eta^6\text{-arene})Ru(pp\text{-}Cl)Cl]^+$ {η^6-arene = C_6H_6 (**1**); *p*-^{i}PrC_6H_4Me (**2**)}, $[(\eta^5\text{-}C_5Me_5)M(pp\text{-}Cl)]^+$ {M = Rh (**3**); Ir (**4**)}, $[(\eta^6\text{-arene})Ru(bppp)Cl]^+$ {η^6-arene = C_6H_6 (**5**); *p*-^{i}PrC_6H_4Me (**6**)}, $[(\eta^5\text{-}C_5Me_5)M(bppp)]^+$ {M =Rh (**7**); Ir (**8**)} as well as the binuclear complexes $[\{(\eta^6\text{-arene})RuCl\}_2(bppp)]^{2+}$ {η^6 -arene =C_6H_6 (**9**); *p*-^{i}PrC_6H_4Me (**10**)} and $[\{(\eta^5\text{-}C_5Me_5)MCl\}_2(bppp)]^{2+}$ {M = Rh (**11**); Ir (**12**)} have been synthesized from 3-chloro-6-(3-pyridyl-1-pyrazolyl)pyridazine (*pp-Cl*) or 3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine (*bppp*) and the corresponding dimers $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ and $[Cp^*M(\mu\text{-}Cl)Cl]_2$, respectively. All complexes were isolated as their hexafluorophosphate salts and characterized by IR, NMR, mass spectrometry and UV-visible spectroscopy. The molecular structures of [**2**]PF_6 and [**7**]PF_6 have been established by single crystal X-ray structure analysis.

Keywords. N-donor ligands; mono and binuclear complexes; ruthenium; rhodium; iridium.

1. Introduction

Mono and binuclear complexes of platinum group metals containing heterocyclic nitrogen based ligands have received considerable attention owing to their catalytic activities[1–7] as well as in the development of new biologically active agents.[8–12] The organometallic complexes of η^6-arene ruthenium,[13,14] and η^5-Cp* half-sandwich complexes of rhodium and iridium have attracted considerable interest as potential anticancer agents.[8–12] Another important aspect, especially from the catalytic perspective involves the design of Ru=O functional groups and analogues capable of reversibly accepting multiple electrons and protons within the relative potential range.[15–17] The capacity to modify their environment in order to induce electronic as well as steric effects will allow fabricating tailored catalysis for specific reactions. Inclusion of the six-membered pyridazine ring in the backbone of *bppp* ligand results in a more pronounced partitioning of the ligand into distinct bidentate domains than in the case with linear polypyridines. This facilitates the formation of mononuclear and binuclear systems. The former has the potential to behave as metallo-ligands in the development of homo/hetero bimetallic systems.[18–21] In the present contribution, we have synthesized new nitrogen based ligands such as 3-chloro-6-(3-pyridyl-1-pyrazolyl)pyridazine (*pp-Cl*) and 3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine (*bppp*) which easily form mono and binuclear complexes with arene ruthenium, Cp* rhodium and Cp* iridium complexes (Cp*= η^5-C_5Me_5). All these new complexes were characterized by elemental analyses, IR, ^{1}H-NMR, UV-Visible and mass spectrometry as well as X-ray crystallographic analyses for some representative complexes. The ligands which are used in the study are shown in chart 1.

2. Experimental

2.1 *General remarks*

All solvents were dried and distilled prior to use. 3,6-dichloropyridazine (Aldrich), acetylpyridine, pyrazole (Aldrich) were purchased and used as received. $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl]_2$, $[(\eta^6\text{-}p\text{-}^i\text{Pr}C_6H_4Me)Ru(\mu\text{-}Cl)Cl]_2$,[22] and $[Cp^*M(\mu\text{-}Cl)Cl]_2$ (M = Rh, Ir)[23] were

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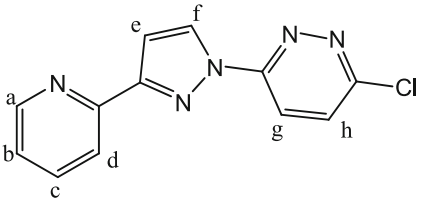
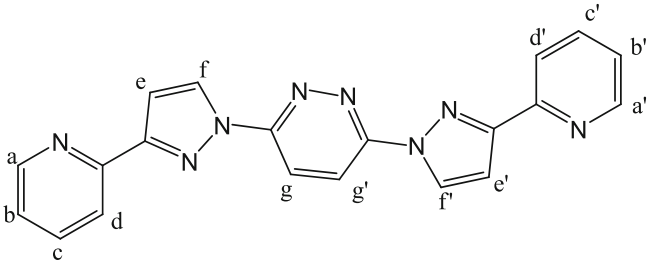


3-Chloro-6-(3-pyridyl-1-pyrazolyl)pyridazine(*pp*-Cl)



3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine (*bppp*)

Chart 1. Ligands used in the study.

prepared according to the literature methods. The 3-(2-pyridyl)-1H-pyrazole (*pypz*) has been prepared by using previously described method.[24] ^{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 mass spectrometer by ESI method. Absorption spectra were obtained at room temperature using a Perkin-Elmer Lambda UV/Visible spectrophotometer.

2.2 *Preparations of ligands: pp-Cl and bppp*

A mixture of 3,6-dichloropyridazine (500 mg, 3.35 mmol), 3-(2-pyridyl)-1H-pyrazole (1 g, 6.88 mmol), potassium carbonate (1.05 g, 7.59 mmol) and tetrabutyl ammonium bromide (1.2 g) in 10 ml of acetone was dissolved. It was stirred and refluxed for 40 h and cooled to room temperature. Then the reaction mixture was poured in to 100 ml of water, resulted in whitish precipitate; it was filtered off, washed with excess water and air dried. It was purified by chromatography on silica gel using chloroform as the eluent to give the analytically pure ligand 3-chloro-6-(3-pyridyl-1-pyrazolyl)pyridazine (*pp-Cl*) (20%) as a pale yellow colour powder and the second fraction was eluted with chloroform/methanol (10:1) give the analytically pure ligand 3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine (*bppp*) (80%) as a colourless solid.

2.2a *3-chloro-6-(3-pyridyl-1-pyrazolyl)pyridazine (pp-Cl)*: Pale yellow solid, yield 120 mg (13%) ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.77 (d, 1H, J = 2.80 Hz, Ha), 8.68 (d, 1H, J = 4.40 Hz, Hf), 8.34 (d, 1H, J = 9.20 Hz, Hg), 8.04 (d, 1H, J = 8.00 Hz, Hh), 7.77 (dt, 1H, J = 1.60 Hz, Hd), 7.63 (d, 1H, J = 9.20 Hz, Hc), 7.28 (dt, 1H, J = 1.60 Hz, Hb), 7.18 (d, 1H, J = 2.40 Hz, He); ESI-MS (m/z): 258.1 (100%) [M+1]; UV–Vis {acetonitrile, λ_{max} nm (ε 10^{-5} M^{-1} cm^{-1})}: 318 (0.37).

2.2b *3,6- Bis(3-pyridyl-1-pyrazolyl)pyridazine (bppp)*: White solid, yield 780 mg (63%) ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.81 (d, 2H, J = 2.40 Hz, $H_{aa'}$), 8.71 (d, 2H, J = 4.40 Hz, $H_{ff'}$), 8.52 (s, 2H, $H_{gg'}$), 8.11 (d, 2H, J = 8.00, $H_{dd'}$), 7.80 (dt, 2H, J = 1.60 Hz, $H_{cc'}$), 7.29 (dt, 2H, J = 1.60 Hz, $H_{bb'}$), 7.21 (d, 2H, J = 2.80 Hz, $H_{ee'}$); ESI-MS (m/z): 367.2 (100%)[M+1]; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1} cm^{-1}$)}: 316 (0.41), 331 (0.33).

2.3 *General procedure for the preparation of the mononuclear complexes [**1**]PF_6–[**2**]PF_6*

A mixture of $[(\eta^6$-arene)Ru(μ-Cl)Cl$]_2$ (arene = C_6H_6 and *p*-^{i}PrC_6H_4Me) (0.07 mmol), ligand *pp-Cl* (0.18 mmol) and 2.5 equivalents of NH_4PF_6 in dry methanol (15 ml) was stirred at room temperature for 6 h. The precipitate was separated by filtration, washed with cold methanol and diethyl ether to remove excess ligand and dried *in vacuo*.

2.3a *[(η^6-C_6H_6)Ru(pp-Cl)Cl]PF_6 ([**1**]PF_6)*: Orange-yellow solid, yield 75 mg (87%) ^{1}H NMR (400 MHz, CD_3CN, δ): 9.55 (d, 1H, J = 5.60 Hz), 8.97 (d, 1H, J = 2.80 Hz), 8.72 (d, 1H, J = 7.28 Hz), 8.45 (m, 2H), 8.32 (t, 1H, J = 7.60 Hz, 7.60 Hz), 7.78 (m, 2H), 5.95 (s, 6H); IR (KBr, cm^{-1}): 1604(m), 1408(s), 844(s) 558(s); ESI-MS (m/z): 472.1 (100%) $[M\text{-}PF_6]^+$; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1} cm^{-1}$)}: 310 (0.19); Anal. Calc. for $C_{18}H_{14}Cl_2F_6N_5PRu$ (617.28): C, 35.02; H, 2.29; N, 11.35. Found: C, 34.72; H, 2.13; N, 11.05%.

2.3b *[(η^6-*p*-^{i}PrC_6H_4Me)Ru(pp-Cl)Cl]PF_6 ([**2**]PF_6)*: Dark orange solid, yield 83 mg (90%) ^{1}H NMR (400 MHz, CD_3CN, δ): 9.22 (d, 1H, J = 5.60 117 Hz), 8.75 (d, 1H, J = 4.80 Hz), 8.62 (d, 1H, J = 3.20 Hz), 8.19–8.12 (m, 3H), 7.66 (dd, 1H, J = 7.60 Hz, 7.60 Hz), 7.40 (d, 1H, J = 3.2 Hz) 5.72 (d, 1H, J = 6.40 Hz, Ar_{p-cy}), 5.46 (d, H, J = 6.00 Hz, Ar_{p-cy}), 5.30 (d, 1H, J = 6.00 Hz, Ar_{p-cy}), 5.18 (d, 1H, J = 6.00 Hz, Ar_{p-cy}), 2.37 (sept, 1H, $CH(CH_3)_2$), 2.17 (s,

3H, $Ar_{p-cy-Me}$), 1.21 (d, 3H, $CH(CH_3)_2$), 1.18 (d, 3H, $CH(CH_3)_2$); IR (KBr, cm^{-1}): 1629(m), 1406(s), 844(s), 763(s), 558(s); ESI-MS (m/z): 527.2 (100%) $[M\text{-}PF_6]^+$; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}cm^{-1}$)}: 309 (0.28); Anal. Calc. for $C_{22}H_{14}Cl_2F_6N_5PRu$ (665.32): C, 39.72; H, 2.12; N, 10.53. Found: C, 39.34; H, 2.01; N, 10.12 %.

2.4 *General procedure for the preparation of the mononuclear complexes [**3**]PF_6 and [**4**]PF_6*

A mixture of $[Cp^*M(\mu\text{-}Cl)Cl]_2$ (M = Rh, Ir) (0.07 mmol), ligand *pp-Cl* (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 during this time dark yellow colour crystalline compound formed. It was separated by filtration, washed with cold methanol and diethyl ether to remove excess ligand and dried *in vacuo*.

2.4a *[Cp*Rh(pp-Cl)Cl]PF_6([**3**]PF_6)*: Dark yellow in colour, yield 86 mg (91%) ^{1}H NMR (400 MHz, CD_3CN, δ): 8.91 (d, 1H, J = 5.20 Hz), 8.67 (d, 1H, J = 4.40 Hz), 8.50 (d, 1H, J = 7.60 Hz), 8.36 (m, 3H), 7.44 (dt, 1H, J = 5.20 Hz, 6.80 Hz), 7.22 (d, 1H, J = 2.4 Hz), 2.15 (s, 15H, C_5Me_5); IR (KBr, cm^{-1}): 1626(m), 1458(s), 845(s), 759(s), 558(s); ESI-MS(m/z): 531.3 (100%) $[M\text{-}PF_6]^+$; UV–Vis {acetonitrile, λ_{max} nm (ε 10^{-5} $M^{-1}cm^{-1}$)}: 316 (0.27); Anal. Calc. for $C_{22}H_{23}Cl_2F_6N_5PRh$ (676.23): C, 39.07; H, 3.43; N, 10.36. Found: C, 38.85; H, 3.24; N, 10.03 %.

2.4b *[Cp*Ir(pp-Cl)Cl]PF_6 ([**4**]PF_6)*: Dark yellow colour, yield 89 mg (88%) ^{1}H NMR (400 MHz, CD_3CN, δ): 9.01 (d, 1H, J = 139 5.60 Hz), 8.71 (d, 1H, J = 4.80 Hz), 8.62 (d, 1H, J = 6.40 Hz), 8.42 (m, 3H), 7.48 (dt, 1H, J = 5.32 Hz, 5.60 Hz), 7.35 (d, 1H, J = 4.80 Hz), 1.88 (s, 15H, C_5Me_5); IR (KBr, cm^{-1}): 1631(m), 1495(s), 845(s), 760(s), 558(s); ESI-MS(m/z): 620.9 (100%) $[M\text{-}PF_6]^+$; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}$ cm^{-1})}: 318 (0.29); Anal. Calc. for $C_{22}H_{23}Cl_2F_6IrN_5P$ (765.54): C, 34.52; H, 3.03; N, 9.15. Found: C, 34.01; H, 2.92; N, 8.95 %.

2.5 *General procedure for the preparation of the mononuclear complexes [**5**]PF_6 –[**6**]PF_6*

A mixture of $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (arene = C_6H_6 and *p*-^{i}PrC_6H_4Me) (0.07 mmol), ligand *bppp* (0.15 mmol) and 2.5 equivalents of NH_4PF_6 in dry methanol (15 ml) was stirred at room temperature for 6 h. The precipitate was separated by filtration, washed with cold methanol and diethyl ether to remove excess ligand and dried *in vacuo*.

2.5a *[(η^6-C_6H_6)Ru(bppp)Cl]PF_6 ([**5**]PF_6)*: Brown colour; yield 85 mg (84%) ^{1}H NMR (400 MHz, CD_3CN, δ): 9.48 (d, 1H, J = 5.20 Hz), 8.68 (d, 1H, J = 5.64 Hz), 8.62 (d, 1H, J = 3.20 Hz), 8.32–8.28 (m, 5H), 7.76 (dt, 2H), 7.62 (t, 1H, J = 3.32 Hz), 7.43 (d,1 H, J = 3.24 Hz), 7.26 (d, 1H, J = 4.20 Hz), 7.20 (d, 1H, J = 4.00 Hz), 5.92 (s, 6H, C_6H_6); IR (cm^{-1}): 1614 (m), 1454 (s), 1437 (s), 844 (s), 788 (s), 558 (s); ESI-MS: 580.9 [M+1], 545.2 [M-Cl]; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5} M^{-1}cm^{-1}$)}: 276 (0.57), 314 (0.92), 417 (0.04); Anal. Calc. for $C_{26}H_{20}ClF_6N_8PRu$ (725.98): C, 43.01; H, 2.78; N, 15.43. Found: C, 42.65; H, 2.65; N, 15.11 %.

2.5b *[(η^6-*p*-^{i}PrC_6H_4Me)Ru(bppp)Cl]PF_6 ([**6**]PF_6)*: Orange-yellow solid; yield 89 mg (83%) ^{1}H NMR (400 MHz, CD_3CN, δ): 9.55 (d, 1H, J = 5.20 Hz), 8.72 (d, 1H, J = 5.64 Hz), 8.68 (d, 1H, J = 3.20 Hz), 8.20–8.18 (m, 4H), 7.68 (dt, 2H), 7.42 (t, 1H, J = 3.32 Hz), 7.38 (d, 1H, J = 4.80 Hz), 7.22 (d, 1H, J = 4.20 Hz), 7.18 (d, 2H, J = 5.60 Hz), 5.72 (d, 1H, J = 6.40 Hz, Ar_{p-cy}), 5.42 (d, 1H, J = 6.00 Hz, Ar_{p-cy}), 5.39 (d, 1H, J = 6.00 Hz, Ar_{p-cy}), 5.29 (d, 1H, J = 5.60 Hz, Ar_{p-cy}), 2.70 (sept, 1H, $CH(CH_3)_2$), 2.33 (s, 3H, $Ar_{p-cy-Me}$), 1.71 (d, 3H, 3 J = 6.20 Hz, $CH(CH_3)_2$), 1.69 (d, 3H, J = 6.80 Hz, $CH(CH_3)_2$); IR (cm^{-1}): 1604(m), 1449(s), 1437(s), 843(s), 783(s), 558(s); ESI-MS: 637.1 [M+1], 602.1 [M-Cl]; UV–Vis {acetonitrile λ_{max} nm ($\varepsilon 10^{-5} M^{-1}$ cm^{-1})}: 274 (0.57), 313 (0.89), 418 (0.05); Anal. Calc. for $C_{30}H_{28}ClF_6N_8PRu$ (782.08): C, 46.07; H, 3.61; N, 14.33. Found: C, 45.64; H, 3.53; N, 14.11 %.

2.6 *General procedure for the preparation of the mononuclear complexes [**7**]PF_6 and [**8**]PF_6*

A mixture of $[Cp^*M(\mu\text{-}Cl)Cl]_2$ (M = Rh, Ir) (0.07 mmol), ligand *bppp* (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 during this time dark yellow colour crystalline compound formed. It was separated by filtration, washed with cold methanol and diethyl ether to remove excess ligand and dried under vacuum.

2.6a *[Cp*Rh(bppp)Cl]PF_6 ([**7**]PF_6)*: Dark yellow colour, yield 96 mg (84%) ^{1}H NMR (400 MHz, CD_3CN, δ): 9.39 (d, 1H, J = 5.20 Hz), 8.68 (d, 1H, J = 5.40 Hz), 8.54 (d, 1H, J = 3.64 Hz), 8.18–8.10

(m, 4H), 7.61 (dt, 2H), 7.48 (d, 1H, $J = 3.60$ Hz), 7.32 (d, 1H, $J = 4.8$ Hz), 7.22 (d, 1H, $J = 4.20$ Hz), 7.16 (d, 2H, $J = 3.64$ Hz), 2.11 (s, 15H, C_5Me_5); ESI-MS (m/z): 639.2 (100%) $[M\text{-}PF_6]^+$; IR (KBr, cm^{-1}): 1626(m), 1458(s), 845(s), 759(s), 558(s); UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5}M^{-1}cm^{-1}$)}: 276 (0.57), 315 (0.87), 419 (0.04); Anal. Calc. for $C_{30}H_{29}ClF_6N_8PRh$ (784.93): C, 45.91; H, 3.72; N, 14.28. Found: C, 45.54; H, 3.63; N, 14.01 %.

2.6b *[(η^5-C_5Me_5)Ir(bppp)Cl]PF_6 ([**8**]PF_6)*: Dark yellow in colour, yield 95 mg (83%) ^{1}H NMR (400 MHz, CD_3CN, δ): 9.40 (d, 1H, $J = 5.32$ Hz), 8.72 (d, 1H, $J = 5.40$ Hz), 8.62 (d, 1H, $J = 3.64$ Hz), 8.20–8.14 (m, 4H), 7.65 (dt, 2H), 7.48 (d, 1H, $J = 3.60$ Hz), 7.31 (d, 1H, $J = 4.8$ Hz), 7.18 (d, 1H, $J = 4.80$ Hz), 7.15 (d, 2H, $J = 3.60$ Hz), 1.98 (s, 15H, C_5Me_5); ESI-MS (m/z): 729.2 (100%) $[M\text{-}PF_6]^+$; IR (KBr, cm^{-1}): 1631(m), 1495(s), 845(s) 760(s), 558(s); UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5}M^{-1}cm^{-1}$)}: 277 (0.58), 314 (0.95), 423 (0.04); Anal. Calc. for $C_{30}H_{29}ClF_6IrN_8P$ (874.24): C, 41.22; H, 3.34; N, 12.82. Found: C, 40.95; H, 3.24; N, 12.65 %.

2.7 *General procedure for the syntheses of the dinuclear complexes [**9**]$(PF_6)_2$ to [**10**]$(PF_6)_2$*

A mixture of [(η^6-arene)Ru(μ-Cl)Cl]$_2$ (arene = C_6H_6 and *p*-^{i}PrC_6H_4Me) (0.10 mmol) and *bppp* (0.10 mmol) was suspended in methanol (20 ml) and stirred at room temperature for 6 h. Then, NH_4PF_6 (46 mg, 0.25 mmol) was added to the reaction mixture and further stirred for 3 h. The precipitate was filtered, washed with methanol and diethylether (3 × 10 ml) and dried *in vacuo*.

2.7a *[{(η^6-C_6H_6)RuCl}$_2$(μ-bppp)]$(PF_6)_2$ ([**9**]$(PF_6)_2$)*: Orange-yellow solid; yield 91 mg (85%) ^{1}H NMR (400 MHz, CD_3CN, δ): 9.34 (d, 2H, $J = 4.20$ Hz), 9.14 (s, 2H), 8.81 (d, 2H, $J = 2.40$ Hz), 8.24 (d, 2H, $J = 6.80$ Hz), 7.72 (t, 2H, $J = 5.60$, 4.80 Hz), 7.50 (d, 2H, $J = 2.40$Hz), 7.36 (d, 2H, $J = 4.80$ Hz), 5.75 (s, 12H, C_6H_6); IR (cm^{-1}): 1614 (m), 1454 (s), 1437 (s), 844 (s), 788 (s), 558 (s); ESI-MS: 940.6$[M^{2+}+PF_6^-]^+$; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5}M^{-1}$ cm^{-1})}: 278 (0.54), 312 (0.83), 408 (0.04); Anal. Calc. for $C_{32}H_{26}Cl_2F_{12}N_8P_2Ru_2$ (1085.58): C, 35.40; H, 2.41; N, 10.32. Found: C, 35.06; H, 2.25; N, 10.02%.

2.7b *[{(η^6-*p*-^{i}PrC_6H_4Me)RuCl}$_2$(μ-bppp)]$(PF_6)_2$ ([**10**]$(PF_6)_2$)*: Orange-yellow solid; yield 99 mg (84%) ^{1}H NMR (400 MHz, CD_3CN, δ): 9.55 (d, 2H, $J = 5.60$ Hz), 9.37 (s, 2H), 9.14 (d, 2H, $J = 2.80$ Hz), 8.52 (d, 2H, $J = 7.60$ Hz), 8.48 (t, 2H, $J = 7.20$, 7.60 Hz), 8.36 (t, 2H), 7.86 (d, 2H, $J = 2.40$ Hz), 6.10 (d, 2H, $J = 6.00$ Hz, Ar_{p-cy}), 5.81 (d, 2H, $J = 6.00$ Hz, Ar_{p-cy}), 5.69 (d, 2H, $J = 6.00$ Hz, Ar_{p-cy}), 5.54 (d, 2H, $J = 6.00$ Hz, Ar_{p-cy}), 2.68 (sept, 2H, $CH(CH_3)_2$), 2.25 (s, 6H, $Ar_{p-cy-Me}$), 1.18 (d, 3H, $J = 6.20$ Hz, $CH(CH_3)_2$), 1.12 (d, 3H, $J = 6.80$ Hz, $CH(CH_3)_2$); IR (cm^{-1}): 1604(m), 1449(s), 1437(s), 843(s), 783(s), 558(s); ESI-MS: 1052.6 $[M^{2+}+PF_6^-]^+$; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5}M^{-1}cm^{-1}$)}: 276 (0.57), 314 (0.91), 410 (0.04); Anal. Calc. for $C_{40}H_{42}Cl_2F_{12}N_8P_2Ru_2$ (1197.79): C, 40.11; H, 3.53; N, 9.36. Found: C, 39.81; H, 3.42; N, 9.12%.

2.8 *General procedure for the syntheses of the dinuclear complexes [**11**]$(PF_6)_2$ to [**12**]$(PF_6)_2$*

A mixture of [Cp*M(μ-Cl)Cl]$_2$ (M = Rh and Ir) (0.10 mmol) and *bppp* (0.10 mmol) was suspended in methanol (20 ml) and refluxed for 5 h. Then, NH_4PF_6 (23 mg, 0.13 mmol) was added to the reaction mixture and further refluxed for an hour. The precipitate observed was filtered, washed with methanol and diethylether (3 × 10 ml) and dried *in vacuo*.

2.8a *[{Cp*RhCl}$_2$(μ-bppp)]$(PF_6)_2$ ([**11**] $(PF_6)_2$)*: Dark yellow colour, yield 101 mg (84%) ^{1}H NMR (400 MHz, CD_3CN, δ): 9.38 (d, 2H, $J = 5.40$ Hz), 9.17 (s, 2H), 8.81 (d, 2H, $J = 2.32$ Hz), 8.24 (d, 2H, $J = 6.80$ Hz), 7.75 (t, 2H, $J = 5.20$, 4.80 Hz), 7.52 (d, 2H, $J = 2.32$ Hz), 7.37 (d, 2H, $J = 4.32$ Hz), 2.05 (s, 30H, C_5Me_5); IR (cm^{-1}): 1604(m), 1449(s), 1437(s), 843(s), 783(s), 558(s); ESI-MS: 1058.6 $[M^{2+}+PF_6^-]^+$; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5}M^{-1}cm^{-1}$)}: 276 (0.39), 314 (0.67), 420 (0.04); Anal. Calc. for $C_{40}H_{44}Cl_2F_{12}N_8P_2Rh_2$ (1203.48): C, 39.92; H, 3.69; N, 9.31. Found: C, 39.65; H, 3.51; N, 9.01%.

2.8b *[{Cp*IrCl}$_2$(μ-bppp)]$(PF_6)_2$ ([**12**] $(PF_6)_2$)*: Dark yellow colour, yield 105 mg (86%) ^{1}H NMR (400 MHz, CD_3CN, δ): 9.31 (d, 2H, $J = 4.36$ Hz), 9.14 (s, 2H), 8.78 (d, 2H, $J = 2.80$ Hz), 8.21 (d, 2H, $J = 6.32$ Hz), 7.72 (t, 2H, $J = 5.60$, 4.80 Hz), 7.50 (d, 2H, $J = 2.40$ Hz), 7.36 (d, 2H, $J = 4.80$ Hz), 1.99 (s, 15H, C_5Me_5); IR (cm^{-1}): 1604(m), 1449(s), 1437(s), 843(s), 783(s), 558(s); ESI-MS: 1236.2 $[M^{2+}+PF_6^-]^+$; UV–Vis {acetonitrile, λ_{max} nm ($\varepsilon 10^{-5}M^{-1}$ cm^{-1})}: 273 (0.46), 313 (0.71), 418 (0.04); Anal. Calc. for

$C_{40}H_{44}Cl_2$ $F_{12}Ir_2N_8P_2$ (1382.1): C, 34.76; H, 3.21; N, 8.11. Found: C, 34.61; H, 3.25; N, 8.01%.

2.9 *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 corresponding complexes. The X-ray intensity data were measured at 293(2) K on a Bruker Apex II CCD area detector employing graphite monochromated using Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å). An empirical absorption correction was made by modelling a transmission surface by spherical harmonics employing equivalent reflections with I>2σ (I) using the program SADBAS.[25] The structures were solved by direct methods using the program SHELXS 97 and refined by full matrix least squares base on F^2 using the program SHELXL-97.[26] The weighting scheme used was $W = 1/[\sigma 2(F_{02}) + 0.0311P_2 + 3.5016\ P]$ where $P = (F_{02} + 2F_{c2})/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a 'riding' model. Refinement converged at a final $R =$ 0.0423 and 0.0454 (for complexes **2** and **7**, respectively, for observed data F^2), and $wR2 = 0.0804$ and 0.0667 (for complexes **2** and **7**, respectively, for unique data F^2). Regarding complex **7** molecular structure, we have encountered two difficulties, they are; (i) one is assigning N(8) and C(17), and another one is (ii) occupancy of the solvent molecule acetonitrile. The matter regarding an ambiguity in assigning N(8) and C(17), exchanging the atoms did not improve the refinement. So the labelling was done in analogy with other compounds and represents the most probable orientation of the molecular fragment. The second factor is now explained on the following lines: the central atom of solvent molecule with occupancy of C is 0.5. 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 consider 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 Å. 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%. Details of crystallographic data collection parameters and refinement are summarized in table 1. Selected bond lengths and angles are given in table 2.

Table 1. Crystallographic and structure refinement parameters for compounds [**1**]PF_6 and [**7**]PF_6.

Complex	[**2**]PF_6	[**7**]PF_6
Chemical formula	$C_{22}H_{22}Cl_2F_6N_5PRu$	$C_{30}H_{29}ClF_6N_8PRh.0.5CH_3CN$
Crystal system	Monoclinic	Monoclinic
Formulae weight	673.39	803.96
Wavelength (Å)	0.71073	0.71073
Space group	C-2/c	P21/*n*
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)	10.1768 (8)	8.5156 (17)
b (Å)	22.7250 (16)	19.095 (4)
c (Å)	22.133 (2)	22.334 (5)
β (°)	97.646 (7)	90.46 (3)
V (Å^3)	5073.2 (7)	3631.5 (13)
Z	8	4
T (K)	293 (2)	293 (2)
D_x (g /cm^3)	1.763	1.470
μ(mm^{-1})	0.959	0.65
Scan range (°)	1.79< θ <24.65	2.11< θ <20.00
Unique reflections	4000	3331
Reflections used [I>2σ(I)]	2291	1042
R_{int}	0.0646	0.189
Final R indices [I>2σ(I)]	0.0423, $wR2$ 0.0803	0.0443, wR_2 0.0626
R indices (all data)	0.0862, $wR2$ 0.0863	0.1881, wR_2 0.0894
Goodness-of-fit	0.824	0.534
Max, Min (e Å^{-3})	0.696, −0.718	0.284, −0.261

Table 2. Selected bond lengths (Å) and angles (°) for compounds [**1**]PF_6 and [**7**]PF_6.

	[**2**]PF_6		[**7**]PF_6
Interatomic distances			
Ru-N1	2.099(3)	Rh-N1	2.08(1)
Ru-N2	2.089(3)	Rh-N2	2.16(5)
Ru-Cl1	2.406(2)	Rh-Cl1	2.396(4)
Ru-centroid (C6 ring)	1.683	Rh-centroid (C5 ring)	1.79
C5-C6	1.351(5)	C5-C6	1.31(1)
N1-C1	1.390(5)	N1-C1	1.39(2)
N2-N3	1.420(5)	N2-N3	1.42(1)
Angles			
N1-Ru-N2	75.50(1)	N1-Rh-N2	73.25(3)
N1-Ru-Cl1	83.80(1)	N1-Rh-Cl1	86.21(3)
N2-Ru-Cl1	84.52(1)	N2-Rh-Cl1	91.47(2)
Ru1-N1-C5	116.90(2)	Rh1-N1-C5	115.21(8)
Ru1-N2-C6	115.50(2)	Rh1-N2-C6	114.72(4)

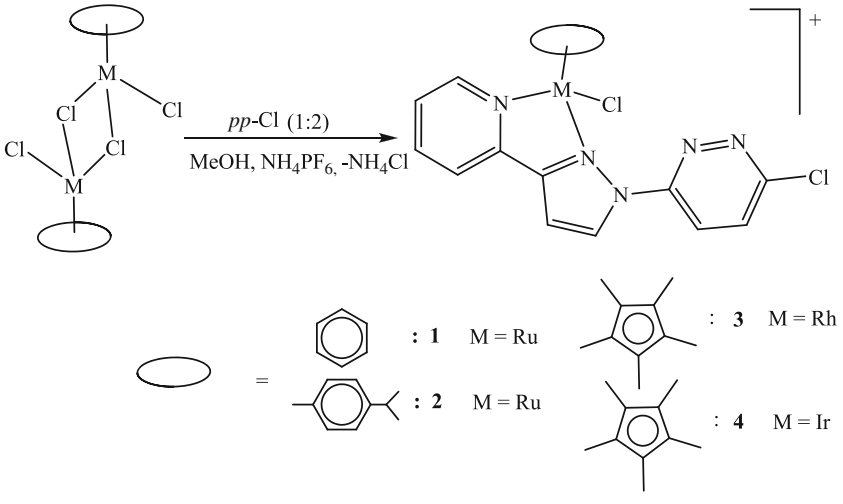
3. Results and discussion

3.1 *Synthesis of ligands*

The ligands 3-chloro-6-(3-pyridyl-1-pyrazolyl)pyridazine (*pp-Cl*) and 3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine were synthesized by the condensation of 3,6-dichloropyridazine and 3-(2-pyridyl)-1H-pyrazole. The reaction was carried out in acetone under refluxing condition in the presence of potassium carbonate and the phase transfer catalyst tetrabutylammonium bromide. The resulting compounds were characterized by spectroscopic methods.

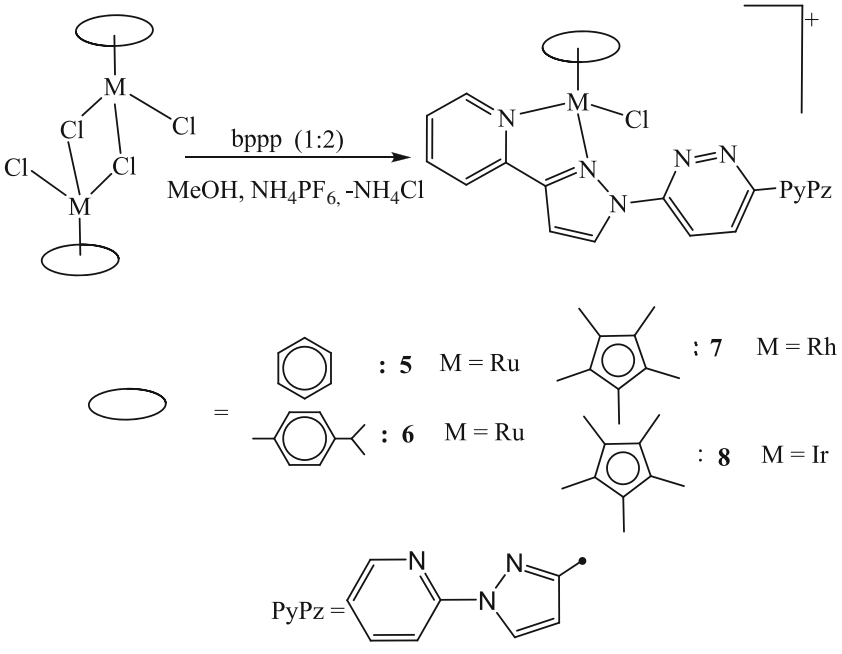
3.2 *Synthesis of the mononuclear complexes [**1**–**8**]PF_6*

The mononuclear cationic arene ruthenium and pentamethylcyclopentadienyl rhodium and iridium complexes having 3-chloro-6-(3-pyridyl-1-pyrazolyl)pyridazine (*pp-Cl*) and 3,6-bis(3-pyridyl-1-pyrazolyl) pyridazine (*bppp*) ligands *viz.*, [(η^6-C_6H_6)RuCl(*pp-Cl*)] PF_6 [**1**]PF_6,[(η^6-*p*-^{i}PrC_6H_4Me)RuCl(*pp-Cl*)]PF_6 [**2**]PF_6, [Cp*RhCl(*pp-Cl*)]PF_6 [**3**]PF_6 and [Cp*IrCl (*pp-Cl*)]PF_6 [**4**]PF_6 (scheme 1) and [(η^6-C_6H_6)RuCl (*bppp*)]PF_6 [**5**]PF_6, [(η^6-*p*-^{i}PrC_6H_4Me)RuCl(*bppp*)] PF_6 [**6**]PF_6, [Cp*RhCl(*bppp*)]PF_6 [**7**]PF_6 and [Cp*



Scheme 1. The mononuclear cationic arene ruthenium and pentamethylcyclopentadienyl rhodium and iridium complexes having (*pp-Cl*) ligand.

IrCl(*bppp*)]PF_6 [**8**]PF_6 (scheme 2) have been prepared by the reaction of arene or pentamethylcyclopentadienyl complexes [(η^6-arene)Ru(μ-Cl)Cl]$_2$ (arene = C_6H_6 and *p*-^{i}PrC_6H_4 Me) and [(Cp*)M(μ-Cl)Cl]$_2$ (M = Rh and Ir) with 2.1 equivalents of ligand 3-chloro-6-(1-pyridyl-3-pyrazolyl)pyridazine (*pp-Cl*) or 3,6-bis(1-pyridyl-3-pyrazolyl)-pyridazine (*bppp*) in methanol. The complexes **1** to **8** were isolated as hexafluorophosphate salts and exhibit an orange–red colour. They are non-hygroscopic, air-stable, shiny crystalline solids sparingly soluble in methanol, dichloromethane and chloroform, but soluble in acetone and acetonitrile. All these metal complexes were fully characterized by IR, NMR and UV-Vis and mass spectrometry. The infrared spectra of the complexes **1** to **8** exhibit a strong band in the region 844–850 cm^{-1}, a typical $\nu_{(P-F)}$ stretching band and for the PF_6 anions as well as bands corresponding phenyl, pyridyl, pyrazolyl and pyridazine (C=C and C=N) rings were observed. The mass spectra of these compounds exhibited the corresponding molecular ion peaks at m/z = 472, 527, 531, 621, 581, 637, 639 and 729. The ^{1}H NMR spectrum of free ligands 3-chloro-6-(3-pyridyl-1-pyrazolyl)pyridazine (*pp-Cl*) exhibits a characteristic set of eight resonances at 8.77 (d, 1H), 8.68 (d, 1H), 8.34 (d, 1H), 8.04 (d, 2H), 7.77 (dt, 1H), 7.63 (d, 2H), 7.28 (dt, 1H), 7.18 (d, 1H) and 3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine (*bppp*) exhibits seven resonances at δ = 8.81 (d, 2H), 8.71 (d, 2H), 8.52 (s, 2H), 8.11 (d, 2H), 7.80 (dt, 2H), 7.29 (dt, 2H), 7.21 (d, 2H) for the pyrazole, pyridazine and pyridine ring protons. Upon coordination with the metal atom, the cationic complexes **1** to **4** exhibit five to six distinct resonances at 8.91 (d, 1H), 8.67 (d, 1H), 8.50 (d, 1H), 8.36 (m, 3H), 7.44 (dt, 1H), 7.22 (d, 1H) which are assignable to pyrazolyl, pyridazine and pyridyl ring protons of the 3-chloro-6-(3-pyridyl-1-pyrazolyl)pyridazine (*pp-Cl*) ligand and complexes **5** to **8** exhibit in between seven and nine distinct resonances at 9.55 (d, 1H), 8.72 (d, 1H), 8.68 (d, 1H), 8.20–8.18 (m, 4H), 7.68 (dt, 2H), 7.42 (t, 1H), 7.38 (d, 1H), 7.22 (d, 1H), 7.18 (d, 2H) which are assignable to pyrazolyl, pyridazine and pyridyl ring protons of the 3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine (*bppp*) ligand, indicating formation of mononuclear complexes. Besides these resonances, complexes **1** and **5** exhibit a singlet at δ = 5.95 and 5.92, respectively for the protons of the benzene ligand. Complexes **2** and **6** exhibits two doublets at δ = 1.71–1.69, as well as a septets at δ = 2.70–2.32 for the protons of the isopropyl group and a singlet at 2.17 ppm for the methyl protons of *p*-cymene ring. The four doublets observed at 5.59–5.39 correspond to the aromatic *p*-cymene ring CH protons. 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 and chiral nature of metal atom.[27–29] Interestingly, the chemical shifts of complex **6** shows downfield compared to complex **2** of *p*-cymene ligand. Complexes **3**, **4**, **7** and **8** exhibit a



Scheme 2. The mononuclear cationic arene ruthenium and pentamethylcyclopentadienyl rhodium and iridium complexes having (*bppp*) ligand.

strong peak at δ = 2.15, 1.88, 2.11 and 1.98 for pentamethylcyclopentadienyl ligand, respectively, which are slightly shifted downfield in comparison to the starting complexes.

3.3 *Crystal structure analysis of [(η^6-p-^{i}PrC$_6$H$_4$Me)Ru(pp-Cl)Cl]PF$_6$ ([**2**]PF$_6$) and [Cp*Rh(bppp)Cl]PF$_6$ ([**7**]PF$_6$)*

The molecular structure of [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru-(*pp-Cl*)Cl]PF$_6$ ([**2**]PF$_6$) and [Cp*Rh(*bppp*)Cl]PF$_6$ [**7**]PF$_6$ have been established by single-crystal X-ray structure analysis. Both complexes shown a typical piano-stool geometry with the metal centre coordinated by the aromatic ligand, chloride and a chelating *N*, *N′*-ligand (see figures 1 and 2).The metal atom is in octahedral arrangement and the *pp-Cl* or *bppp* ligand is found to coordinate through the N1 atom of the pyridine moiety and the N2 atom of the pyrazolyl ring to generate a five-membered ring metallo-cycle (see figures 1 and 2). In these complexes, the N atom of pyridazine points away from the metal centre and show no interaction with neighbouring cations. Selected bond lengths and angles for complexes **2** and **7** are presented in table 2. In the mononuclear complex **2** the N1-metal [2.099(3) Å] distance of the pyridyl ring is slightly longer than the corresponding pyrazolyl, N2-metal distance [2.089(3) Å], in contrast, for complex **7** the N1-metal [2.082(1) Å] distance slightly shorter than the corresponding pyrazolyl N2-metal distance [2.161(5) Å], which are comparable to those in [(η^6-C$_6$Me$_6$)RuCl(C$_5$H$_4$N-2-CH=N=C$_6$H$_4$-*p*-NO$_2$)]PF$_6$[30], [Ru(mes)Cl{C$_5$H$_4$N-2-C(Me)=N(CHMePh)}]BF$_4$[31], [Cp*RhCl(C$_5$H$_4$N-2-CH=N=C$_6$H$_4$-*p*-NO$_2$)]BF$_4$[32], [(η^6-C$_6$H$_6$)Ru(2-(2-thiazolyl)-1,8-naphthyridine)Cl]PF$_6$,[27] [(η^6-*p*-^{i}PrC$_6$H$_4$Me) RuCl(2,3-bis (2-pyridyl)pyrazine)]BF$_4$.[33] While the M-Cl [2.406(2) Å and 2.396(4) Å] bond lengths show no significant differences in all the cations and reported values.[34–37] The N(1)–M(1)–N(2) bond angle in complex **2** and **7** is found to be [75.1(1)°] and [73.2(3)°], respectively, which are similar to those of complexes [(η^6-*p*-^{i}PrC$_6$H$_4$Me)RuCl(2,3-bis(2-pyridyl) pyrazine)]$^+$ [N(1)–Ru(1)–N(2) = 76.5(2)°][33] and [(η^6-*p*-^{i}PrC$_6$H$_4$Me)RuCl(2,3-bis(2-pyridyl)quinoxaline)]$^+$.[37] The distances between the ruthenium atom and the centroid of the (η^6-*p*-^{i}PrC$_6$H$_4$Me) ring is 1.683 Å in complex **2**, whereas the distance between the rhodium atom and the centroid of the η^5-C$_5$Me$_5$ ring is 1.781 Å in complex **7**. These bond distances are comparable to those in the related complex cations [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(pyNp)Cl]PF$_6$, [Cp*Ir(pyNp)Cl]PF$_6$ (PyNp=2-(2-pyridyl)-1,8-naphthyridine) (1.79 Å)[27] and [Cp*Rh(3,6-bis(2-pyridyl)-4-phenylpyridazine)Cl]PF$_6$ (1.789 Å).

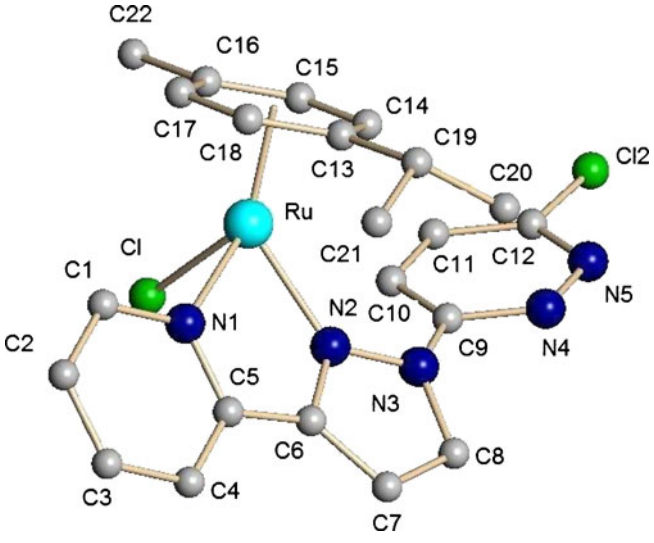


Figure 1. Molecular structure of complex **2**. Hydrogen atoms and anion are omitted for clarity.

3.4 *Synthesis of the dinuclear complexes [**9**–**12**](PF$_6$)$_2$*

The reaction of the dimeric chloro complexes [(η^6-arene)Ru(μ-Cl)Cl]$_2$ (arene = C$_6$H$_6$,*p*-^{i}PrC$_6$H$_4$Me) and [Cp*M(μ-Cl)Cl]$_2$ (M = Rh, Ir) with 1 equivalent of 3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine (*bppp*) in methanol results in the formation of the orange colour, air-stable dinuclear complexes [{(η^6-C$_6$Me$_6$)RuCl}$_2$(*bppp*)](PF$_6$)$_2$ [**9**](PF$_6$)$_2$, [{(η^6-*p*-^{i}PrC$_6$H$_4$Me)RuCl}$_2$(*bppp*)](PF$_6$)$_2$ [**10**](PF$_6$)$_2$, [{Cp*RhCl}$_2$((*bppp*)](PF$_6$)$_2$ [**11**](PF$_6$)$_2$ and [{Cp*IrCl}$_2$((*bppp*)](PF$_6$)$_2$ [**12**](PF$_6$)$_2$. All these complexes are isolated as their hexafluorophosphate salts (scheme 3) and they were characterized by IR, Mass, ^{1}H-NMR spectrometry and elemental analysis. Infrared spectra of these dinuclear complexes **9** to **12**, showed a similar trend to the mononuclear cationic complexes **1** to **8**. In the mass spectra the complexes **7**, **8**, **11** and **12** hexafluorophosphate salts give rise to two main peaks; a minor peak with an approximately 50% intensity attributed to [M^{2+}+PF$_6^-$]$^+$ at m/z 940, 1052, 1058 and 1236, respectively and a major peak which corresponds to loss of [(arene)MCl]$^+$ fragment to the formation of mononuclear cations **5**–**8** at m/z = 580, 637, 739 and 729, respectively. The ^{1}H NMR spectra of the dinuclear cationic complexes **9** to **12** exhibit seven distinct resonances at 9.55 (d, 2H), 9.37 (s, 2H), 9.14 (d, 2H), 8.52 (d, 2H), 8.48 (t, 2H), 8.36 (t, 2H), 7.86 (d, 2H) which are assignable

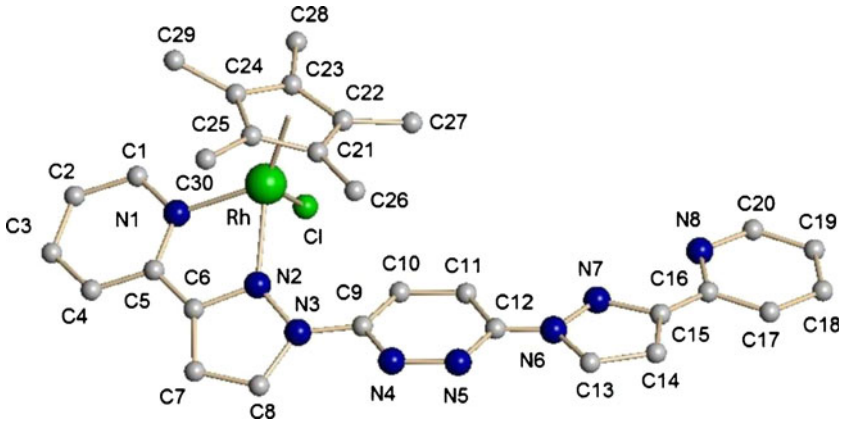
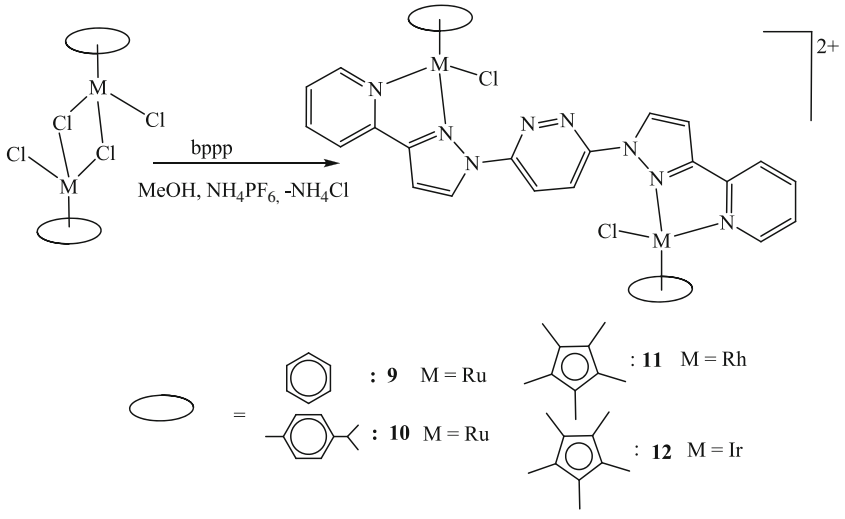


Figure 2. Molecular structure of complex **7**. All hydrogen atoms, solvent molecule and anion are omitted for clarity.

to pyridine, pyrazole and pyridazine ring protons of the 3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine (*bppp*) ligand. The chemical shift of the *bppp* ligand protons upon complex formation shifted down field with reference to free ligand. However, $H_{ff'}$ protons of metal bounded pyrazoles shifted up field compared to $H_{gg'}$ unbound pyridazine protons of *bppp* ligand up on complexation; this may be due to the metal to ligand charge transfer in all these complexes (figure 3). Besides these *bppp* ligand resonances complex **9** exhibits a singlet at $\delta =$ 5.75 for the two benzene rings and complex **10** exhibits two doublets at $\delta = 1.18$–1.12, and septet at $\delta = 2.68$ for the protons of the isopropyl group and a singlet at $\delta = 2.25$ for the methyl protons of *p*-cymene ring. The four doublets observed at $\delta = 6.10$–5.54 correspond to the aromatic *p*-cymene ring CH protons. Interestingly, the chemical shift of these protons as well as methyl protons shifted downfield significantly with reference to starting precursor ranging from $\delta = 5.20$ to 5.42 and mono nuclear complexes (figure 3). This could be due to the increased steric nature on the *p*-cymene ring in dinuclear complexes compared to mono nuclear compounds. Complexes **11** and **12** exhibit a strong peak at $\delta = 2.05$ and 1.99 for the protons of pentamethylcyclopentadienyl ligands, respectively which are slightly shifted downfield in comparison to the starting complexes. Due to lack of formation of single crystals of these complexes, we are assigned by NMR spectral data, these are dinuclear complexes bridged by the ligand *bppp* and formation of dicationic complexes.

3.5 *UV-visible spectroscopy*

Electronic absorption spectra of compounds *pp-Cl*, *bppp* and complexes **1** to **12** were acquired in acetonitrile, at 10^{-5} M concentration in the range of



Scheme 3. The dinuclear cationic arene ruthenium and pentamethylcyclopentadienyl rhodium, iridium complexes having (*bppp*) ligand.

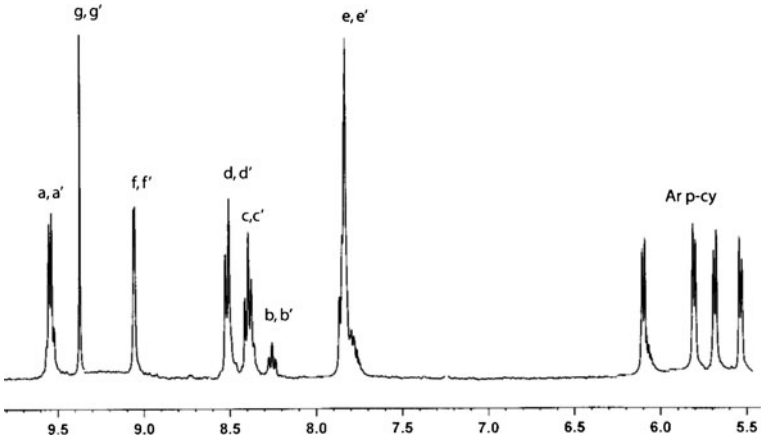


Figure 3. ^{1}H-NMR spectrum of complex **10** in CDCl3, represents *bppp* ligand resonances and *p*-cymene ligand aromatic protons (isopropyl protons are omitted for clarity).

220–550 nm. The spectral data are well-formulated in experimental section. The spectrum of the ligand 3-chloro-6-(3-pyridyl-1-pyrazolyl)pyridazine (*pp-Cl*) exhibits a band at 318 nm, while ligand 3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine (*bppp*) exhibits two bands at 316 nm and 331 nm as a shoulder peak, 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) $d\pi(M) \rightarrow \pi^*$ (L - ligand) bands in the visible region.[38] Since the low spin d^6 configuration of the mononuclear complexes provides filled orbitals of proper symmetry at the Ru(II),Rh(III) and Ir(III) centres, these can interact with low-lying π^* orbitals of the ligands. All the mononuclear complexes **1** to **4** show only an intense band in the region of 308–316 nm, while complexes **5** to **8** shown three bands at 276–278 nm, 312–314 nm and a broad peak at 417–423 nm. Whereas the dinuclear complexes **9** to **12** show three bands, which are almost similar to complexes **5** to **8** at 274 to 276 nm as a shoulder peak at 312–314 nm as a high intense peak and a broad band at 418–420 nm. The high intensity band in UV region for both mononuclear and dinuclear complexes is assigned to inter and intra-ligand π–π^*/ n–π^* transitions,[39–41] while the low energy absorption band in the visible region for all complexes is assigned to metal-to-ligand charge transfer (MLCT) (t_{2g}–π^*). Representative spectra of these complexes are represented in figure 4.

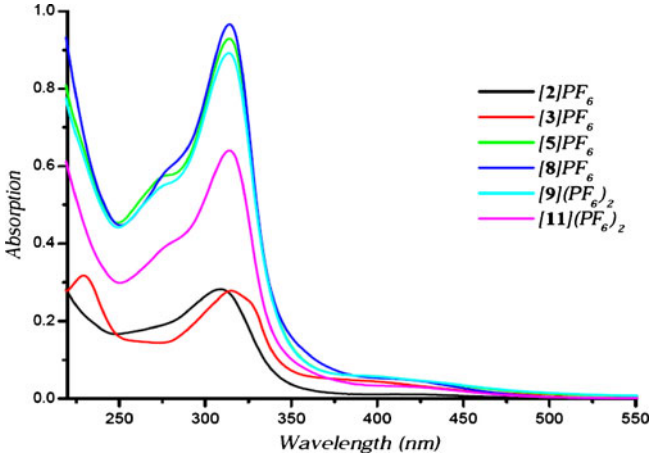


Figure 4. UV-visible electronic spectra of representative complexes in acetonitrile at 298 K.

4. Conclusions

In summary, we have prepared two novel chelating ligands 3-chloro-6-(3-pyridyl-1-pyrazolyl)pyridazine (*pp-Cl*) and 3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine (*bppp*). Ligands *pp-Cl* and *bppp* reacted with series of arene ruthenium and Cp* rhodium and iridium complexes giving new series of mononuclear and binuclear complexes. However, we were unable to get single crystals of dinuclear complexes, which were characterized by other spectral techniques.

Supplementary data

CCDC-**749700** [**2**]PF_6 and CCDC-**749701** [**7**]PF_6 contain the crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif or by e-mailing data request@ccdc.cam.ac.uk, or by contacting: The Cambridge Crystallographic Data Centre, 12 Union

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