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η^5 and η^6 - cyclic π-perimeter hydrocarbon platinum group metal complexes of 3-(2-pyridyl)pyrazole derived ligands with a pendant nitrile group: Syntheses, spectral and structural studies

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Abstract. Reaction of two equivalents 4-{(3-(pyridine-2-yl) 1H-pyrazole-1-yl}methyl benzonitrile (**L1**) and 3-{(3-(pyridine-2-yl)1H-pyrazole-1-yl}methyl benzonitrile (**L2**) with one equivalent of [(η^6-arene)Ru(μ-Cl)Cl]$_2$ and [Cp*M(μ-Cl)Cl]$_2$ in methanol yielded mononuclear complexes of the formulae [(η^6-arene)Ru(**L1/L2**)Cl]BF_4{arene =C_6H_6 (**1**, **6**); $C_{10}H_{14}$ (**2**, **7**); C_6Me_6 (**3**, **8**)} and [Cp*M(**L1/L2**)Cl]PF_6/BF_4 {Cp*= η^5-C_5Me_5, M=Rh (**4**, **8**); Ir (**5**, **10**)}. These complexes are characterized by IR, ^{1}H NMR and identities of the structure are established by single crystal XRD studies of some of the representative complexes. It is confirmed from the spectral studies that the nitrile group is not taking part in complexation; instead it remains as a free pendant group only.

Keywords. Arene; pentamethylcyclopentadienyl; ruthenium; rhodium; 3-(2-pyridyl)pyrazole.

1. Introduction

When the strong σ-donor properties of the pyrazole group and the π-accepting ability of the pyridyl ring linked together in a single ligand system, it gives rise to properties or situation which is entirely different from the isolated pyrazole or the pyridyl group being able to form a stable five-membered ring metal complexes.[1,2] 3-(2-pyridyl)pyrazole and pyridyl-triazole ligands linked by a spacer provides a great potential to isolate mono- or polynuclear complexes. They play an important role in construction of complexes with various structures including multi-nuclear discrete molecules as well as 1D and 2D coordination polymers exhibiting interesting properties.[3–8] The copper(I) complex of 1-benzyl-[3-(2-pyridyl)]pyrazole has the ability of non-enzymatic hydrolysis of an inactivated ester $MeCO_2Et$ as reported by Mukherjee *et al*.[9] The formation of mixed metal complexes in a hierarchical step-wise manner have been reported with the pyridyl–pyrazole derived ligands viz., 4-((3-(pyridine-2-yl) 1H-pyrazole-1-yl) methyl benzonitrile and 4-((3-(pyridine-2-yl) 1H-pyrazole-1-yl) methyl naphthonitrile. These ligands react with Ag(I) salts to give a range of infinite coordination networks or dimeric 'boxes' in which the pyrazolyl-pyridine chelates and the aromatic nitrile groups both participate in coordination to Ag(I) ions.[3] Although there have been some reports of the complexes of η^6 and η^5 –platinum group metal complexes with pyridyl–pyrazole derived ligands,[10,11] complexes derived from 3-(2-pyridyl)pyrazole with a pendant nitrile group have not yet been explored. The nitrile group being an electron-rich centre, it has the possibility to bind with a metal ion through the nitrogen atom. η^6 and η^5 –platinum group metal complexes containing nitrogen-based ligands have importance in biological systems[12,13] and the pyridyl–pyrazole derived ligands have the possibility to form mixed metal complexes. With this background, the ligands 4-((3-(pyridine-2-yl) 1H-pyrazole-1-yl)methyl benzonitrile and 3-((3-(pyridine-2-yl)1H-pyrazole-1-yl)methyl benzonitrile are synthesized and studied the formation of the metal complexes. The structures of the ligands used in this work are shown below in scheme 1.

We report here ten new mononuclear complexes of η^6 and η^5–cyclichydrocarbon platinum group metal complexes derived from the mentioned ligands but an attempt to synthesize dinuclear complexes by varying the ligand to metal ratio have not been successful. Thus,

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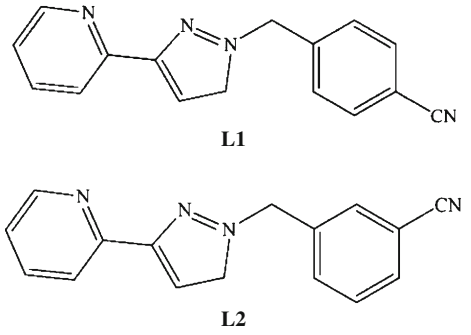


Scheme 1. Ligands used in the study.

the ligand coordinates to the metal through the pyridine nitrogen and one of the pyrazole or pyrazolate nitrogens giving rise to a five-membered ring complexes leaving the nitrile group uncoordinated.

2. Experimental

2.1 *General remarks*

Infrared spectra were recorded on a Perkin-Elmer Model 983 spectrophotometer with the sample prepared as KBr pellets. The NMR spectra were obtained using Bruker Avance II 400 spectrometer in $CDCl_3$ and acetone-d_6 depending on the solubility of the complexes using TMS as an internal standard. Elemental Analysis of the complexes was performed on a Perkin-Elmer 2400 CHN/S analyser. All chemicals used were of reagent grade. All reactions were carried out in dried and distilled solvents. The ligands 4-((3-(pyridine-2-yl) 1H-pyrazole-1-yl)methylbenzonitrile (**L1**) and 3-((3-(pyridine-2-yl)1H-pyrazole-1-yl)methyl benzonitrile (**L2**)[3] and the precursor complexes were prepared following the literature procedures.[14–18]

2.2 *Single crystal X-ray diffraction studies*

X-ray quality crystals were obtained from chloroform (complex **4**), and acetone/hexane (complexes **6** and **9**) as an orange plate, yellow rod and yellow needle. The crystallizations were done at room temperature. The intensity data for complexes **6** and **9** were collected on a STOE IPDS II diffractometer with MoK_α radiation. A numerical absorption correction was based on the crystal shape that was originally derived from the optical face indexing but was later optimized against equivalent reflections using the STOE X-shape software.[19] The intensity data of **4** was collected with a Bruker SMART APEX II CCD diffractometer equipped with a fine focus 1.75 kW sealed with increasing ω (width of 0.3^0 per frame). The SMART[20] software was used for data acquisition. Data integration and reduction were undertaken with the SAINT[20] software. Structures were refined with full matrix least squares on F^2 using SHELXL-97.[21] All non-hydrogen atoms were refined anisotropically. Structural illustrations have been drawn with ORTEP-3[22] for windows. The ORTEP presentations of the representative complexes have been shown in figures 1, 2, and 3. The data collection parameters are presented in table 1.

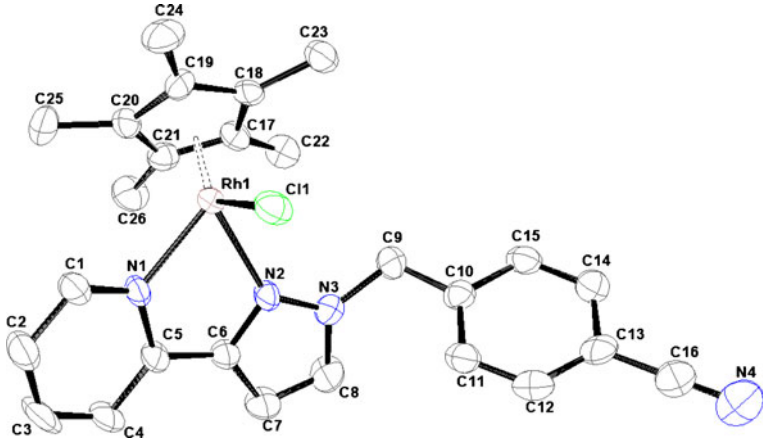


Figure 1. Molecular structure of complex **4** at 35% probability level. Hydrogen atoms, PF_6^- and solvent of crystallization have been omitted for clarity. Selected bond lengths (in Å) and bond angles (°): Rh(1)-Centroid 1.778; N(1)-Rh(1) 2.125(5); N(2)-Rh(1) 2.117(5); Cl(1)-Rh(1) 2.390(17); N(2)-Rh(1)-N(6) 75.28(19); N(2)-Rh(1)-Cl(1) 90.25(14); N(1)-Rh(1)-Cl(1) 90.10(14).

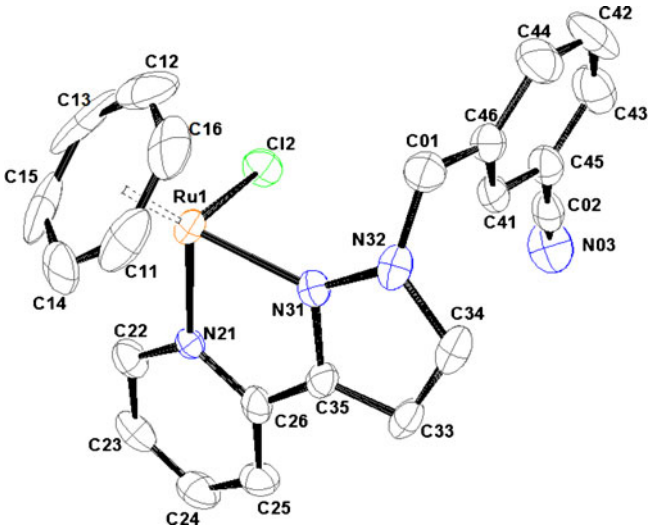


Figure 2. Molecular structure of complex **6** at 35% probability level. Hydrogen atoms and BF_4^- have been omitted for clarity. Selected bond lengths (in Å) and bond angles (°): Ru(1)-Centroid 1.673; Ru(1)-N(21) 2.101(2); Ru(1)-N(31) 2.048(3); Ru(1)-Cl(2) 2.3817(19); N(21)-Ru(1)-N(31) 75.57(13); N(21)-Ru(1)-Cl(2) 84.39(8); N(31)-Ru(1)-Cl(2) 85.82(12).

2.3 *Preparation of [(η^6-arene)Ru(L1)Cl]BF_4 {arene =C_6H_6(1), $C_{10}H_{14}$(**2**), C_6Me_6(**3**)} and [(Cp*M(**L1**)Cl]PF_6/ BF_4 {M=Rh (**4**), Ir (**5**)}*

A mixture of [(η^6-arene)Ru(μ-Cl)Cl]$_2$ (0.048 mmol) or [Cp*M(μ-Cl)Cl]$_2$ (0.048 mmol) and the ligand **L1** (20 mg, 0.096 mmol) and two equivalents of the respective salts (NH_4PF_6 for complex **4** and NH_4BF_4 for rest of the complexes) were stirred in dry methanol (15 ml) for overnight to ensure complete reaction. The yellowish brown and the yellowish precipitate obtained in case of **1** and **4** respectively were centrifuged, washed with diethyl ether several times and dried under vacuum. In the case of **2**, **3** and **5**, the orange yellow solution obtained was evaporated under reduced pressure. The residue was then extracted with dichloromethane, precipitated out with diethyl ether and washed several times with the same and dried under vacuum.

2.3a *Complex **1***: Yield: 30 mg (70%). Anal. Calcd. for $C_{22}H_{18}BClF_4N_4Ru$ (%) : C, 47.01; H, 3.22; N, 9.97. Found (%): C, 46.87; H, 3.11; N, 9.78; IR (KBr pellets, cm^{-1}): 2230 (s, $\nu_{C\equiv N}$), 1069 (s, ν_{B-F}); ^{1}H NMR (400 MHz, acetone-d_6): δ=9.594 (d, J=5.6 Hz, 1H, pyridyl); 8.279 (t, J=5.6 Hz, 2H, pyridyl); 8.168 (d, J=2.8 Hz, 1H, pyridyl) 7.877 (d, J=8.4 Hz, 1H, pyrazolyl); 7.682 (m, J=2.4 Hz, 8 Hz, 4H, phenyl); 7.364 (d, J=2.8 Hz, 1H, pyrazolyl); 6.342 (s, 6H, benzene); 6.264 (d, J=16 Hz, 1H, $-CH_2$-); 6.15 (d, J=15.6 Hz, 1H, -CH_2).

2.3b *Complex **2***: Yield: 38 mg (59%). Anal. Calcd for $C_{26}H_{26}BClF_4N_4Ru$ (%): C, 50.53; H, 4.24; N, 9.06. Found (%) : C, 49.33; H, 3.89; N, 8.76; IR (KBr pellets, cm^{-1}): 2236 (s, $\nu_{C\equiv N}$); 1082 (s, ν_{B-F}); ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.50 (d, J=5.6 Hz, 1H, pyridyl); 8.28 (m, J=6.4 Hz, 1.2 Hz, 2H, pyridyl); 8.18 (d, J=2.8 Hz, 1H, pyridyl); 7.866 (d, J=8.4 Hz, 1H, pyrazolyl); 7.667 (m, J=2.0 Hz, 8.4 Hz, 4H, phenyl); 7.37 (d, J=2.8 Hz, 1H, pyrazolyl; 6.342 (d, J=6.4 Hz, 1H, Ar_{p-cym}); 6.27 (d, J=6.4 Hz, 1H, Ar_{p-cym}); 6.218 (d, J=15.6 Hz, 1H, -CH_2-); 6.13 (d, J=15.6 Hz, 1H, -CH_2); 6.079 (d, J=6 Hz, 1H, Ar_{p-cym}); 6.014 (d, J=6 Hz, 1H, Ar_{p-cym}); 2.65 (sept, J=6.8 Hz, 1H, C*H*$(CH_3)_2$); 2.30 (s, 3H, -CH_3); 1.023 (dd, J=1.2 Hz, 6H, $CH(CH_3)_2$).

2.3c *Complex **3***: Yield: 38 mg (72%). Anal. Calcd. for $C_{28}H_{30}BClF_4N_4Ru$ (%) : C, 52.05; H, 4.68; N, 8.67. Found (%): C, 51.93; H, 4.65; N, 8.10; IR (KBr pellets, cm^{-1}): 2234 (s, $\nu_{C\equiv N}$); 1082 (s, ν_{B-F}); ^{1}H NMR (400 MHz, $CDCl_3$): δ =8.696 (d, J=5.2 Hz, 1H, pyridyl); 8.020 (t, J=7.2 Hz, 2H, pyridyl); 7.865 (d, J=7.6 Hz, 1H, pyridyl); 7.776 (d, J=2.8 Hz, 1H, pyrazolyl); 7.571 (m, J=9.2 Hz, 11.6 Hz, 4H,

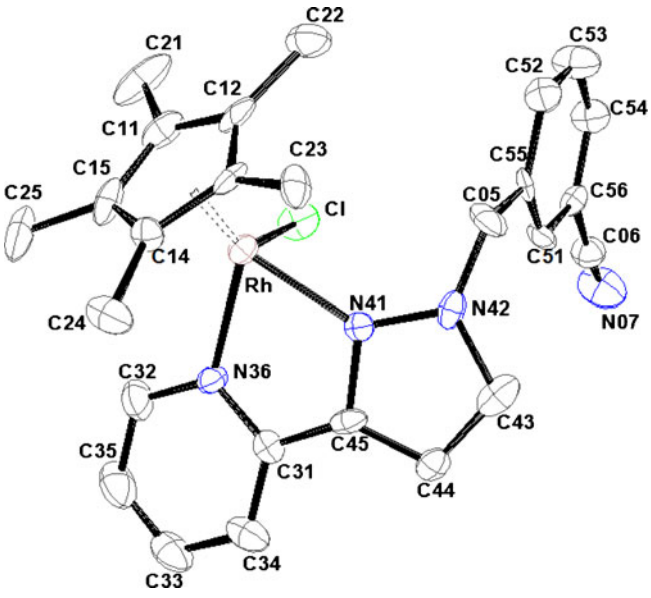


Figure 3. Molecular structure of complex **9** at 35% probability level. Hydrogen atoms and BF_4^- have been omitted for clarity. Selected bond lengths (in Å) and bond angles (°): Rh-Centroid 1.797; Rh-N(36) 2.131(4); Rh-N(41) 2.092(3); Rh-Cl 2.373(2); N(41)-Rh(1)-N(36) 74.9(2); N(41)-Rh-Cl 89.01(12); N(36)-Rh-Cl 92.79(14).

Table 1. Crystallographic and structure refinement parameters for complexes **4**. $CHCl_3$, **6** and **9**.

Chemical formula	$C_{27}H_{28}Cl_4F_6N_4PRh$	$C_{22}H_{18}BClF_4N_4Ru$	$C_{26}H_{27}BClF_4N_4Rh$
Formula weight	798.21	561.73	620.69
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P_{2(1)2(1)2(1)}$	P2(1)/n	P_{bca}
Crystal colour	Orange Plate	Yellow Rod	Yellow needle
Crystal size (mm^3)	0.34 × 0.20 × 0.14	0.32 × 0.15 × 0.13	0.31 × 0.11 ×0.10
a(Å)	9.3593(4)	11.359(2)	16.250(3)
b(Å)	15.8047(7)	11.451(2)	14.680(3)
c(Å)	22.2165(10)	17.309(4)	21.649(4)
$\beta(^0)$	90.00	100.41 (3)	90.00
V ($Å^3$)	3286.3(3)	2214.2(8)	5164.4(17)
Z	4	4	8
T (K)	296 (2)	293(2)	293 (2)
D_c ($g.cm^{-3}$)	1.613	1.685	1.597
μ (mm^{-1})	0.953	0.880	0.817
Scan range (°)	1.58–25.00	2.124–25.92	2.09–24.65
Unique reflections	30436	10800	23046
R_{int}	0.1317	0.0630	0.1612
Final R indices [I>2σ(I)]*	0.0470, wR_2 0.0903	0.0464, wR_2 0.1150	0.0405, wR_2 0.0502
R indices (all data)	0.0771, wR_2 0.0986	0.1201, wR_2 0.1467	0.1638, wR_2 0.0706
Goodness-of-fit	0.846	0.537	0.600
Max, Min $\Delta\rho$/e ($Å^{-3}$)	0.963, −0.791	0.852, −0.525	0.431, −0.520

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

phenyl); 6.907 (d, J=2.8 Hz, 1H, pyrazolyl); 5.9439 d, J=14 Hz, 1H, -CH_2-); 5.549 (d, J=14.6 Hz, 1H, -CH_2-); 2.115 (s, 18H, C_6Me_6).

2.3d *Complex **4***: Yield: 35 mg (62%). Anal. Calcd. for $C_{26}H_{27}PClF_6N_4Rh$ (%): C, 45.93; H, 4.00; N, 8.24. Found (%) : C, 45.76; H, 3.91; N, 7.93; IR (KBr pellets, cm^{-1}) 2235 (s, $\nu_{C\equiv N}$); 844 (s, ν_{P-F}); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.753 (d, J=1.4 Hz, 1H, pyridyl); 8.086 (t, J=1.9 Hz, 2H, pyridyl); 7.899 (d, J=7.6 Hz, 1H, pyrazolyl); 7.631 (m, J=7.6 Hz, 4H, phenyl); 6.920 (d, J=1.4 Hz, 1H, pyrazolyl); 5.899 (d, J=13.6 Hz, 1H, -CH_2-); 5.661 (d, J=14 Hz, 1H, -CH_2-) 1.70 (s, 15H, Cp*).

2.3e *Complex **5***: Yield: 33 mg (61%). Anal. Calcd. for $C_{26}H_{27}BClF_4N_4Ir$ (%): C, 43.91; H, 3.82; N, 7.87. Found (%) : C, 43.03; H, 3.51; N, 7.60; IR (KBr pellets, cm^{-1}) 2236 (s, $\nu_{C\equiv N}$); 1082 (s, ν_{B-F}); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.738 (d, J=5.6 Hz, 1H, pyridyl); 8.084 (t, J=7.6 Hz, 2H, pyridyl); 8.029 (d, J=8.0 Hz, 1H, pyridyl); 7.693 (d, J=8.4 Hz, 1H, pyrazolyl); 7.640 (m, J=10.8 Hz, 4H, phenyl); 6.995 (d, J=1.4 Hz, 1H, pyrazolyl); 6.045 (d, J=14 Hz, 1H, -CH_2-); 5.619 (d, J=14 Hz, 1H, -CH_2-); 1.719 (s, 15H, Cp*).

2.4 *Preparation of [(η^6-arene)Ru(**L2**)Cl]BF_4 {arene =C_6H_6 (**6**), $C_{10}H_{14}$ (**7**), C_6Me_6 (**8**)} and [Cp*M(**L2**)Cl]BF_4 {M=Rh (**9**), Ir (**10**)}*

The syntheses of these complexes [**6**–**10**] are similar to that of the complexes described above. The ligand used in synthesizing these complexes was prepared following the literature procedure and reporting for the first time. The analytical data for the ligand and the complexes are given below:

2.4a *Ligand **L2***: Yield: 700 mg (78%). Anal. Calcd. for $C_{16}H_{12}N_4$ (%): C, 73.83; H, 4.64; N, 21.52. Found (%) : C, 73.23; H, 4.55; N, 21.35; IR (KBr pellets, cm^{-1}) 2236 (s, $\nu_{C\equiv N}$); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.641 (d, J=4.4 Hz, 1H, pyridyl); 7.930 (d, J=8.0 Hz, 1H, pyridyl); 7.731 (dt, J=7.2 Hz, 1.2 Hz, 1H, pyridyl); 7.596 (d, J=3.6 Hz, 1H, pyrazolyl); 7.518 (s, 1H, phenyl); 7.473 (m, J=2.0 Hz, 5.6 Hz, 3H, phenyl); 7.222 (t, J=6.0 Hz, 1H, pyridyl); 6.962 (d, J=2.0 Hz, 1H, pyrazolyl); 5.431 (s, 2H, -CH_2-).

2.4b *Complex* ***6***: Yield: 35 mg (81%). Anal. Calcd. for $C_{22}H_{18}BClF_4N_4Ru$ (%): C 47.01; H 3.22; N 9.97. Found (%) : C, 46.93; H, 2.97; N, 9.96; IR (KBr pellets, cm^{-1}): 2236 (s, $\nu_{C\equiv N}$), 1082 (s, ν_{B-F}); ^1H NMR (400 MHz, acetone-d_6): δ = 9.598 (d, J=5.6 Hz, 1H, pyridyl); 8.264 (m, J=5.6 Hz, 2H, pyridyl); 8.176 (d, J=2.8 Hz, 1H, pyridyl); 7.884 (s, 1H, phenyl); 7.844 (t, J=6.8 Hz, 1H, pyridyl); 7.690 (m, J=4.0 Hz, 3H, phenyl); 7.351 (d, J=2.8 Hz, 1H, pyrazolyl); 6.376 (s, 6H, benzene); 6.239 (d, J=14 Hz, 1H, -CH_2-); 6.130 (d, J=14 Hz, 1H, -CH_2-).

2.4c *Complex* ***7***: Yield: 30 mg (63%). Anal. Calcd. for $C_{26}H_{26}BClF_4N_4Ru$ (%): C 50.53; H 4.24; N 9.06. Found (%) : C, 50.13; H, 4.15; N, 9.00; IR (KBr pellets, cm^{-1}): 2235 (s, $\nu_{C\equiv N}$); 1082 (s, ν_{B-F}); 1H NMR (400 MHz, $CDCl_3$): δ= 9.126 (d, J=2.8 Hz, 1H, pyridyl); 7.970 (d, J=5.6 Hz, 1H, pyridyl); 7.805 (m, J=5.6 Hz, 1.2 Hz, 2H, pyridyl); 7.591 (d, J=2.8 Hz, 1H, pyrazolyl); 7.487 (m, J=2.4 Hz, 8 Hz, 3H, phenyl); 7.052 (d, J=2.8 Hz, 1H, pyrazolyl); 6.819 (s, 1H, phenyl); 6.117 (d, J=14.0 Hz, 1H, -CH_2-); 5.805 9d, J=14 Hz, 1H, -CH_2-); 5.411 (d, J=5.6 Hz, 2H, Ar_{p-cym}); 5.275 (d, J=6Hz, 2H, Ar_{p-cym}); 2.516 (sept, J=6.8Hz, 1H, -C*H*$(CH_3)_2$); 2.177 (s, 1H, -CH_3); 1.183 (m, J=7.2Hz, 3.2Hz, 6H, -CH$(CH_3)_2$).

2.4d *Complex* ***8***: Yield: 37 mg (75%). Anal. Calcd. for $C_{28}H_{30}BClF_4N_4Ru$ (%) : C, 52.05; H, 4.68; N, 8.67. Found (%) : C, 51.76; H, 4.57; N, 8.64; IR (KBr pellets, cm^{-1}): 2237 (s, $\nu_{C\equiv N}$); 1069 (s, ν_{B-F}); ^1H NMR (400 MHz, $CDCl_3$): δ= 8.704 (d, J=5.2 Hz, 1H, pyridyl); 8.025 (t, J=6.8 Hz, 2H, pyridyl); 7.935 (d, J=12.0 Hz, 1H, pyridyl); 7.653 (d, J=8.0 Hz, 1H, pyrazolyl); 7.552 (d, J=7.6 Hz, 1H, pyrazolyl); 7.343 (m, J=1.2 Hz, 4 Hz, 3H, phenyl); 6.976 (s, 1H, phenyl); 6.161 (d, J=14.0 Hz, 1H, -CH_2-); 5.523 (d, J=16.0 Hz, 1H, -CH_2-); 2.125 (s, 18H, C_6 Me_6).

2.4e *Complex* ***9***: Yield: 35 mg (73%). Anal. Calcd. for $C_{26}H_{27}BClF_4N_4Rh$ (%) : C, 50.31; H, 4.38; N, 9.02. Found (%) : C, 50.21; H, 4.20; N, 8.937; IR (KBr pellets, cm^{-1}) 2236 (s, $\nu_{C\equiv N}$); 1075 (s, ν_{B-F}); ^1H NMR (400 MHz, $CDCl_3$): δ= 8.757 (d,J=5.2 Hz, 1H, pyridyl); 8.088 (t, J=8.0 Hz, 2H, pyridyl); 7.926 (d, J=8.0 Hz, 1H, pyridyl); 7.809 (d, J=2.4 Hz, 1H, pyrazolyl); 7.682 (d, J=8.0 Hz, 1H, pyrazolyl); 7.622 (m, J=8.4 Hz, 13.2Hz, 3H, phenyl); 6.953 (s, 1H, phenyl); 6.059 (d, J=14.4 Hz, 1H, -CH_2-); 5.633 (d, J=14.4 Hz, 1H, -CH_2-); 1.713 (s, 15H, Cp*).

2.4f *Complex* ***10***: Yield: 37 mg (78%). Anal. Calcd. for $C_{26}H_{27}BClF_4N_4Ir$ (%) : C 43.98; H 3.83; N 7.89. Found (%): C, 43.90; H, 3.53; N, 7.54; IR (KBr pellets, cm^{-1}) 2236 (s, $\nu_{C\equiv N}$); 1076 (s, ν_{B-F}); ^1H NMR (400 MHz, $CDCl_3$): δ= 8.745 (d, J=4.8 Hz, 1H, pyridyl); 8.071 (m, J=7.2 Hz, 6.4 Hz, 3H, pyridyl); 7.768 (d, J=7.6 Hz, 1H, pyrazolyl); 7.691 (d, J=7.6 Hz, 1H, pyrazolyl); 7.605 (m, J=6.8 Hz, 7.6 Hz, 3H, phenyl); 7.010 (s, 1H, phenyl); 6.008 (d, J=11.2 Hz, 1H, -CH_2-); 5.622 (d, J=11.2 Hz, 1H, -CH_2-); 1.723 (s, 15H, Cp*).

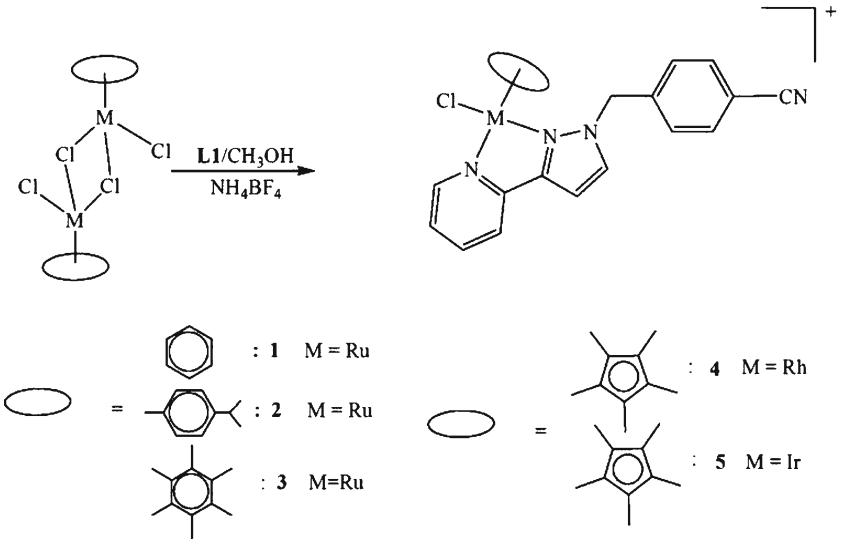
3. Results and discussion

3.1 *General accounts*

Reactions of chloro-bridged dimers viz., $[(\eta^6$-arene)Ru(μ-Cl)Cl$]_2$ and $[Cp^*M(\mu$-Cl)Cl$]_2$ with two equivalents of the ligands **L1** and **L2** in dried methanol followed by the addition of NH_4BF_4 or NH_4PF_6 result in the formation of mononuclear complexes of the formulation $[(\eta^6$-arene)Ru(**L1/L2**)Cl$]BF_4$ and $[Cp^*M$(**L1/L2**)Cl$]BF_4/PF_6$. The reaction takes place through chloro-bridge cleavage followed by the dissociation of one chloride ligand of the mentioned starting precursors as shown in schemes 2 and 3. These complexes are air stable, non-hygroscopic, readily soluble in dichloromethane, acetone and sparingly soluble in chloroform but are insoluble in low boiling non-polar solvents like hexane, diethyl ether and petroleum ether.

3.2 *Infrared studies*

The infrared spectra of the complexes **1**–**10** show a sharp peak at around 2236 cm^{-1} which accounts for nitrile stretching. When compared to the stretching frequency of the nitrile group of the free ligands which is 2236 cm^{-1} for both the ligands, it is found that the position of the $\nu_{(C\equiv N)}$ remains unaltered. This suggests that the metal centre has been coordinated only through the pyridyl–pyrazole unit leaving the pendant nitrile group free and only a monomeric product is formed. These types of ligands have the possibility to bind the metal centre to the pendant nitrile; but in our case, binding of metal centre to it does not occur although we have tried to carry out the reactions by varying the metal to ligand ratios and the reaction conditions. In addition to these observations, the IR spectra indicate ionic nature of these complexes by the display of a sharp stretching frequency of $\nu_{(B-F)}$ *ca.* 1080 cm^{-1} corresponding to BF_4^- counter ion except that of complex **4** which shows

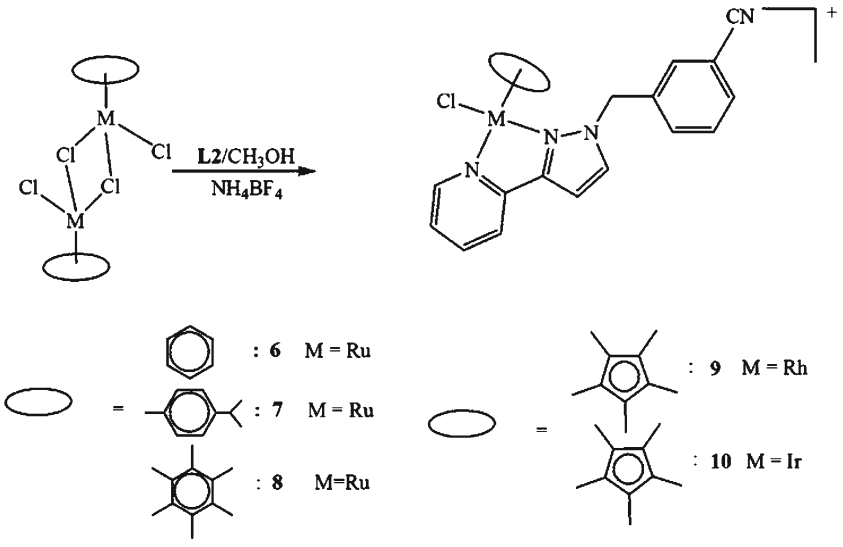


Scheme 2. Reactions of $[(\eta^6\text{-arene/(Cp*)M}(\mu\text{-Cl)Cl}]_2$ with **L1** 1:2 molar ratio.

at around 840 cm^{-1} of $\nu_{(P-F)}$ for the PF_6^- counter ion. The formations of the mononuclear complexes are further confirmed from the ^{1}H NMR as well as the single crystal XRD studies.

3.3 *^{1}H NMR Studies*

3.3a *$[(\eta^6$-Arene)Ru(**L1/L2**)Cl]BF_4*: The ^{1}H NMR spectra of all these six complexes show a downfield shift of the ligand peaks upon coordination with the metal atom as compared to the signals of the free ligands. The ligand peaks resonate in the region ranging from 9.598 to 6.130 ppm for the complexes **1** and **6**. The two doublets at 9.594, 8.168 and a triplet at 8.279 ppm in the spectrum of complex **1** and doublets at 9.598 ppm, 8.176 ppm, multiplet at around 8.264 ppm and a triplet at 7.884 ppm in the spectrum of complex **6** are assigned for the protons of the pyridyl moiety of the respective complexes. The methylene protons show two doublets at 6.264 and 6.150 ppm for complex **1** and 6.239 and 6.130 ppm for complex **6**. Similarly, complexes **2**, **3**, **7** and **8** show similar trends of the ligand protons being shifted to downfield and two doublets have been observed for the methylene protons instead of the expected singlet. Apart from these ligand peaks, the benzene ligand shows a singlet representing six protons with a chemical shift value of 6.342 and



Scheme 3. Reactions of $[(\eta^6\text{-arene/(Cp*)M}(\mu\text{-Cl)Cl}]_2$ with **L2** 1:2 molar ratio.

6.239 ppm respectively for complexes **1** and **6**. Similarly, the hexamethylbenzene ligand in complexes **3** and **8** shows one singlet in which each singlet represents eighteen protons at 2.115 and 2.125 ppm. But complexes **2** and **7** respectively exhibit a septet at 2.650 and 2.516 ppm for the methine proton of the isopropyl group, singlet at 2.300 and 2.177 ppm for the methyl group of the *p*-cymene ligand. The ring protons and the methyl protons of the isopropyl group of the *p*-cymene ligand have shown unusual pattern of resonances. For instance, the methyl protons of the isopropyl group show doubly doublet at 1.023 ppm for complex **2** and multiplet at around 1.183 ppm for complex **7** instead of the doublet as observed in the starting precursor. The aromatic protons of the complex **2** show four doublets in the range of 6.342–6.014 ppm instead of the expected two doublets. These unusual patterns are due to the diastereotopic methyl protons of the isopropyl and aromatic protons of the *p*-cymene ligand owing to the stereogenecity of the ruthenium center after being coordinated to the nitrogen centres.[23,24] However, the aromatic protons of the *p*-cymene in complex **7** exhibit two doublets at 5.411 and 5.275 ppm as in the starting precursors.

Apart from these, almost all the arene protons except for complex **7** exhibit downfield shift as compared to the respective precursors. The main compelling factor for this is the change in electron density on the metal center due to linkage through the nitrogen centres of the ligand. In all these six complexes the signal of the two methylene protons of the ligand shown as two doublets with very high J value (geminal coupling constant) instead of the expected singlet due to the presence of diastereotopic protons which are non-inter convertable on the NMR time scale otherwise a singlet would have been observed.

3.3b *[(Cp*)M(L1/L2)Cl]PF_6/BF_4 where M= Rh or Ir*: The chemical shifts of the ligand protons are shifted downfield being in the range of 8.753–5.661 ppm, 8.738–5.619 ppm, δ 8.757–5.633 ppm and 8.745–5.622 ppm for complexes **4**, **5**, **9** and **10**, respectively as in the case of the above mentioned complexes. In addition to the ligand peaks, these complexes display a singlet at around 1.70 ppm for the fifteen protons of the pentamethylcyclopentadienyl group which is shifted downfield as compared to the starting precursors due to the change in electron density around the metal centre. These complexes also exhibit two doublets with large J value for the two diastereotopic methylene protons of the ligand. This is due to the rigidity of the metal bound pyrazolyl arm and show up as an AB spin system.[25]

3.4 *Molecular structures*

In order to confirm the identity of the ligand (**L2**) as well as the complexes, single crystals of some of the representative complexes have been grown as orange plate (**4**), yellow rod (**6**) and yellow needle (**9**) and analysed. Due to poor quality of the crystal, we are unable to obtain presentable data of complex **1**, so we are presenting only the ORTEP structure of it (figure 4) which is drawn with the available data set just to show the formation of [(η^6-arene)Ru(**L1**)Cl]BF_4. Details about the data collection, refinement and structure solution are recorded in table 1. The cations exhibit the expected and usual pseudo-octahedral half-sandwich 'piano-stool' disposition around the metal atom with the arene or pentamethylcyclopentadienyl ligand occupying one face of the octahedron. The two nitrogens of the bidentate 3-(2-pyridyl)pyrazole moiety and the chloride ion are coordinated to the metal on the other

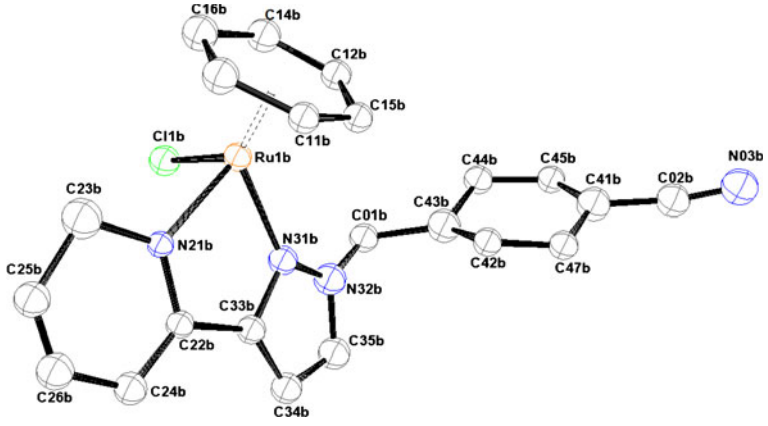


Figure 4. Molecular structure of complex **1** at 35% probability level. Hydrogen atoms and BF_4^- have been omitted for clarity.

face. The molecular structure of the representative complexes are shown below in figures 1, 2, 3 and 4. Complex **4** is found to crystallize in space group $P_{2(1)2(1)2(1)}$ (orthorhombic) with a molecule of chloroform per asymmetric unit while complexes **6** and **9** are found to crystallize in space groups P2(1)/n (monoclinic) and P_{bca} (orthorhombic), respectively. Some of the selected bond lengths and bond angles of complexes **4**, **6** and **9** are given in caption of figures 1, 2, and 3 respectively.

The Rh(1)-Centroid, N(1)-Rh(1), N(2)-Rh(1), Cl(1)-Rh(1) in complex **4** are 1.778, 2.125(5), 2.117(5), 2.390(17) Å, respectively. Whereas in complex **9**, the Rh-centroid, Rh-N (36), Rh-N(41), and Rh-Cl are 1.797, 2.131(4), 2.092(3) and 2.373(2) Å, respectively. A comparative study reveals that the metal-pyridyl nitrogen bond distance in **4** is shorter than that of the metal-pyridyl nitrogen in complex **9** by a unit of 0.025 Å which is indicative of the fact that the pyridyl nitrogen of ligand **L1** binds stronger than that of the ligand **L2** while the metal-pyrazolyl nitrogen bond distance in complex **4** is longer than in **9** by a unit 0.025 Å i.e., pyrazolyl nitrogen of ligand **L2** binds better than that of ligand **L1**. In complex **6**, the Ru(1)-centroid, Ru(1)-Cl(2), Ru(1)-N(21) and Ru(1)-N(31) bond lengths are in the range 1.673 Å, 2.3817(19), 2.048(3) and 2.101(2) Å, respectively which is within the range of reported literatures.[26] Since we are unable to obtain a good quality single crystal for representative complex [(η^6-arene)Ru(**L1**)Cl]BF_4, comparative study could not be carried out in this system. However, we can take into account that the pyrazole nitrogen binds better than the pyridyl nitrogen in all the complexes. The selected bond angles given in the tables are also within the range of reported literatures.[11,26] The N–Ru–N angles have values of 75.28(19), 75.57(13) and 74.9(2)° deviated from 90° as per demand of the bite of the ligand which is in accordance with the literature value of the platinum group pyridyl pyrazole complexes.[26]

4. Conclusions

In conclusion, we are able to synthesize ten new η^5 and η^6—platinum group metal complexes bearing pyridyl–pyrazole ligand with a pendant nitrile group. Syntheses of dinuclear complexes by varying the ligand to metal ratio do not yield the expected dinuclear complexes. Instead, the reaction gives only the monomeric complexes leaving the pendant nitrile group free. The reaction of these ligands with the η^5-cyclopentadienyl and indenyl containing precursors does not yield any products due to decomposition.

5. Supplementary material

CCDC- **838442** (**4**), **838443** (**6**) and **838444** (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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