Half-sandwich pentamethylcyclopentadienyl group 9 metal complexes of 2-aminopyridyl ligands: Synthesis, spectral and molecular study

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Abstract. The reaction of $[\text{Cp}^*\text{M}(\mu\text{-Cl})\text{Cl}]_2$ ($\text{M} = \text{Rh}, \text{Ir}$) with 2-aminopyridyl based ligands lead to the formation of mononuclear neutral complexes of general formula $[\text{Cp}^*\text{MCl}_2(\text{L})]$ {where $\text{L1} = 2\text{-aminopyridine}$, $\text{L2} = 2\text{-amino-3-picoline}$, $\text{L3} = 2\text{-amino-3-nitropyridine}$, and $\text{L4} = 2\text{-amino-3-pyridine carboxyaldehyde}$ }. The complexes have been characterized by FT-IR, UV-Vis, ^1H - ^{13}C NMR and mass spectroscopic methods. X-ray crystallographic studies of the complexes have shown typical piano-stool geometry around the metal centre in which 2-aminopyridyl ligand acts as an N-monodentate ligand and the amino functionality is not involved in metal coordination. The intra/intermolecular arrangement is due to hydrogen bonding.

Keywords. Rhodium; Iridium; 2-aminopyridine; 2-amino-3-picoline; 2-amino-3-nitropyridine.

1. Introduction

Among various N-containing heterocyclic ligands, 2-aminopyridyl ligand has received much attention because of their potentially ambidentate nature and pharmacological properties. These ligands bind to a metal ion in a variety of bonding modes such as a monodentate N-pyridine ligand as well as bidentate ligand and these compounds play an important role in biology. Metal complexes of these ligands have exhibited antibacterial and anti-fungal activity as indicated by recent literature.^{1–3}

Some of the transition metal complexes incorporated with 2-aminopyridyl derivatives have been studied extensively in various applications such as potential anticancer agents and as catalysts. For example, 2-aminopyridine rhodium(I) complexes have been found to be effective catalysts for the homogeneous hydrogenation of olefins⁴ and 2-aminopicoline rhodium(I) was useful in olefin or alkyne hydroacylation and in carbon-carbon bond activation.⁵ The mononuclear ruthenium complexes of chiral auxiliary ligands, 2-amino-(4R)-phenyl-2-oxazoline (amphox), indanyl-2-amino-(4R,5S)-2-oxazoline (aminox) are active catalysts for both transfer of hydrogenation and [4+2] cycloaddition chemistry.⁶

Analysis of cell growth inhibition caused by ruthenium complexes of 2-pyridyl and derivatives on panel

of tumour cell lines (HeLa, B16, MDA-MB-361, MDA-MB-453 and LS-174) revealed low anti-proliferative activity. Replacement of substituted pyridine ligand in complexes such as picolinic acid exhibits better DNA binding affinity and cytotoxicity.^{7–10}

Till now, a few reports are available for metal complexes with the 2-aminopyridine ligands, in which it serves as either a monodentate ligand or a bridging ligand.^{11–13} However, there are no reports dealing with half-sandwich Rh and Ir complexes with these ligands. In the present contribution, we would like to report syntheses of a series of new mononuclear half-sandwich complexes of $\text{Cp}^*\text{Rh(III)}$ and $\text{Cp}^*\text{Ir(III)}$ with 2-aminopyridine ligand L1, L2, L3 and L4 respectively and their characterization by suitable techniques.

2. Experimental

2.1 Physical methods and materials

All reagents were purchased from commercial sources and used as received. $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ and $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ were purchased from Arora Matthey limited, 2-aminopyridine, 2-amino-3-picoline were obtained from Aldrich and 2-amino-3-nitropyridine, 2-amino-3-pyridine carboxyaldehyde were acquired from Merck. The solvents were purified and dried according to standard procedures.¹⁴ All the experiments were performed under normal conditions. The dinuclear metal precursors

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Table 1. Crystallographic and structure refinement parameters for selected complexes.

	3	4	5	6	8
Chemical formula	C16H23Cl2N2Rh	C16H23Cl2IrN2	C15H20Cl2N3O2Rh	C15H20Cl2IrN3O2	C16H21Cl2IrN2O
Formula Mass	417.17	506.46	448.15	537.44	520.45
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
<i>a</i> /Å	11.912(2)	11.908(2)	7.3892(15)	7.5125(15)	7.5416(15)
<i>b</i> /Å	8.4318(17)	8.4938(17)	15.071(3)	15.018(3)	13.907(3)
<i>c</i> /Å	17.051(3)	17.194(3)	31.125(6)	30.912(6)	9.0916(18)
α /°	90.00	90.00	90.00	90.00	90.00
β /°	96.14(3)	96.42(3)	90.00	90.00	113.68(3)
γ /°	90.00	90.00	90.00	90.00	90.00
Unit cell volume/Å ³	1702.7(6)	1728.1(6)	3466.2(12)	3487.6(12)	873.3(3)
Temperature/K	293(2)	293(2)	293(2)	293(2)	293(2)
Space group	P21/c	P21/c	Pbca	Pbca	P21
<i>Z</i>	4	4	8	8	2
Index ranges	$-12 \leq h \leq 14$ $-10 \leq k \leq 5$ $-16 \leq l \leq 21$	$-14 \leq h \leq 14$ $-10 \leq k \leq 10$ $-21 \leq l \leq 11$	$-8 \leq h \leq 8$ $-17 \leq k \leq 17$ $-36 \leq l \leq 36$	$-9 \leq h \leq 9$ $-18 \leq k \leq 16$ $-38 \leq l \leq 34$	$-8 \leq h \leq 8$ $-16 \leq k \leq 16$ $-10 \leq l \leq 10$
<i>D_c</i> (g.cm ⁻³)	1.627	1.947	1.718	2.047	1.979
μ (mm ⁻¹)	1.312	8.031	1.305	7.975	7.953
F(000)	848	976	1808	2064	500
Reflections collected	6347	7223	76975	11472	16390
Independent reflections	3481 [R(int) = 0.0245]	3527 [R(int) = 0.0240]	2993 [R(int) = 0.0276]	3559 [R(int) = 0.0286]	3559 [R(int) = 0.0504]
Completeness to $\theta = 25.00^\circ$	99.8	99.8	99.8	99.8	99.8
Data/restraints/parameters	3481/0/197	3527/0/197	2993/0/213	3559/0/213	2998/0/151
Goodness-of-fit on F ²	1.055	1.042	1.044	1.362	1.044
Final R indices [<i>I</i> > 2 σ (<i>I</i>)]*	0.0278, wR ₂ = 0.0638	0.0278, wR ₂ = 0.0650	0.0206, wR ₂ = 0.0464	0.0499, wR ₂ = 0.0796	0.0243, wR ₂ = 0.0576
R indices (all data)	0.0357, wR ₂ = 0.0638	0.0341, wR ₂ = 0.0675	0.0295, wR ₂ = 0.0485	0.0576, wR ₂ = 0.0796	0.0271, wR ₂ = 0.0584
Max, Min $\Delta\rho/e$ (Å ⁻³)	0.582, -0.771	1.257, -1.205	0.342, -0.280	1.496, -2.877	1.310, -0.757

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

[Cp*M(μ -Cl)Cl]₂ (M = Rh and Ir) were prepared according to literature methods.^{15–17} NMR spectra are recorded on a Bruker Avance II 400 MHz. Infrared spectra were recorded as KBr pellets on a Perkin- Elmer 983 spectrophotometer. Mass spectra were obtained from Water ZQ-4000 mass spectrometer by ESI method in positive mode. Elemental analyses were performed on a Perkin-Elmer-2400 CH/N analyzer. Absorption spectra were obtained at room temperature using a Perkin- Elmer Lambda 25 UV/ visible spectrophotometer.

2.2 Single-crystal X-ray structures analyses

The orange crystals of complexes **3**, **4**, **5**, **6**, **7** and **8** were obtained by slow diffusion method of hexane diffused into DCM solution of the corresponding complexes. Single crystal X-ray diffraction measurements were carried out on an Xcalibur, Eos, Gemini and STOE IPDSII diffractometer. Single crystals picked up from the samples were analyzed on a STOE IPDSII diffractometer using MoK α radiation in the whole reciprocal sphere. A numerical absorption correction was based on the crystal shape originally determined by optical face indexing but later optimized against equivalent reflections using the STOE X-Shape software. Crystal structures were determined and solved using the SHELX software.^{18,19} Crystallographic details are summarized in table 1 and bond lengths and angles were presented table 2. Figure 1 were drawn with ORTEP-3²⁰ and figures 2–3 were drawn with MERCURY.²¹

2.3 General procedure for the preparation of mononuclear complexes **1** to **8**

A mixture of metal precursor [Cp*M(μ -Cl)Cl]₂ (0.1 mmol), 2-aminopyridyl ligand (0.2 mmol) were dissolved in methanol (20 mL) and stirred at room temperature. Yellow coloured precipitate formed immediately.

Further reaction mixture was stirred for further two hours to complete the reaction. The precipitate was washed with methanol, diethyl ether (3 x 10 mL) and dried in vacuum.

2.3a [Cp*RhCl₂(L1)] (1): Red orange solid, Yield 60 mg (76%). IR (KBr, cm⁻¹): 3383(s), 3270(m), 3179(m), 2962(w), 1626(s), 1606(w), 1485(m), 1443(m), 1376(w), 1256(w), 1155(w), 1023(m), 842(m), 786(s); ¹H NMR (400 MHz, CDCl₃) δ 8.49 (d, 1H, H_{JJ} = 5, py ring), 7.25 (d, 1H, H_{JJ} = 4.5, py ring), 6.62 (t, 1H, py ring), 6.49 (t, 1H, py ring), 6.12 (b, 2H, NH₂), 1.57 (s, 15H, Cp* ring); ¹³C NMR (400 MHz, DMSO-d₆+ CDCl₃) δ 8.50, 87.84, 101.21, 113.76, 135.34, 156.82; ESI-MS: 404.06 [M⁺] peak; UV-Vis {Acetonitrile, $\lambda_{\max}$ nm ($\epsilon/10^{-4}$ M⁻¹ cm⁻¹)}: 231(0.43), 295(0.12), 401(0.03). Anal. Calc. for C₁₅H₂₁N₂Cl₂Rh (403.15): C, 44.69; H, 5.25; N, 6.95. Found: C, 44.80; H, 5.42; N, 7.01.

2.3b [Cp*IrCl₂(L1)] (2): Yellow solid, Yield 80 mg (80%). IR (KBr, cm⁻¹): 3373(s), 3282(s), 3183(m), 2968(w), 1623(s), 1607(w), 1488(s), 1433(m), 1377(m), 1253(m), 1157(w), 1123(m), 1053(m), 842(m), 786(s), 612(m); ¹H NMR (400 MHz, CDCl₃) δ 8.48 (d, 1H, H_{JJ} = 4.5, py ring), 7.20 (d, 1H, H_{JJ} = 4.25, py ring), 6.60 (t, 1H, py ring), 6.45 (t, 1H, py ring), 6.10 (b, 2H, NH₂), 1.40 (s, 15H, Cp* ring); ¹³C NMR (400 MHz, DMSO-d₆+ CDCl₃) δ 8.20, 88.11, 101.98, 113.01, 132.86, 154.96; ESI-MS: 493.72 [M⁺] peak; UV-Vis {Acetonitrile, $\lambda_{\max}$ nm ($\epsilon/10^{-4}$ M⁻¹ cm⁻¹)}: 231(0.40), 296(0.19). Anal. Calc. for C₁₅H₂₁N₂Cl₂Ir (492.46): C, 36.58; H, 4.30; N, 5.69. Found: C, 36.70; H, 4.45; N, 5.78.

2.3c [Cp*RhCl₂(L2)] (3): Red orange solid, Yield 79 mg (94%). IR (KBr, cm⁻¹): 3406(s), 3276(s), 3183(m), 2916(w), 1615(s), 1595(w), 1474(s), 1455(m), 1377(m), 1253(m), 1303(w), 1272(w), 1205(w), 1086(w),

Table 2. Selected bond lengths (Å) and angles (°).

Complex	(3)	(4)	(5)	(6)	(8)
M(1)-Cl(1)	2.450(7)	2.4467(12)	2.4020(7)	2.398(2)	2.370(6)
M(1)-Cl(2)	2.4036(7)	2.4084(12)	2.4249(7)	2.418(2)	2.448 (6)
M(1)-N(1)	2.168(2)	2.148(4)	2.2043(19)	2.174(6)	2.2153(19)
M(1)-C _{ave}	2.153(3)	2.154(5)	2.148(2)	2.146(8)	2.244(3)
M(1)-CNT	1.776	1.773	1.770	1.765	1.775
Cl(1)-M(1)- Cl(2)	90.00(3)	87.45(5)	89.59(3)	87.33(8)	88.57(9)
N(1)-M(1)-Cl(1)	93.33(6)	88.32(5)	88.51(5)	87.24(18)	95.15(18)
N(1)-M(1)-Cl(2)	89.77(6)	91.76(10)	93.96(5)	92.58(18)	84.46(16)

CNT represents the centroid of the Cp* ring; C_{ave} represents the average bond distance centroid of the Cp* ring carbon and metal atom.

Figure 1. ORTEP diagram of complexes $[\text{Cp}^*\text{RhCl}_2(\text{L}_2)]$ (3), $[\text{Cp}^*\text{IrCl}_2(\text{L}_2)]$ (4), $[\text{Cp}^*\text{RhCl}_2(\text{L}_3)]$ (5), $[\text{Cp}^*\text{IrCl}_2(\text{L}_3)]$ (6) $[\text{Cp}^*\text{RhCl}_2(\text{L}_4)]$ (7) and $[\text{Cp}^*\text{IrCl}_2(\text{L}_4)]$ (8) with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

1025(m), 789(s), 758(w), 612(m); ^1H NMR (400 MHz, CDCl_3) δ 8.52 (d, 1H, $H_{\text{HJ}} = 5.25$, py ring), 7.29 (d, 1H, $H_{\text{HJ}} = 4.75$, py ring), 6.56 (t, 1H, py ring), 6.14 (b, 2H, NH_2), 2.12 (s, 3H, CH_3), 1.57 (s, 15H, Cp^* ring); ^{13}C NMR (400 MHz, $\text{DMSO}-d_6 + \text{CDCl}_3$) δ 8.49, 88.96, 99.03, 114.24, 135.65, 153.32; ESI-MS: 418.10 $[\text{M}^+]$ peak; UV-Vis {Acetonitrile, λ_{max} nm ($\epsilon/10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$)}: 230(0.74), 297(0.26), 405(0.06). Anal. Calc. for $\text{C}_{16}\text{H}_{23}\text{N}_2\text{Cl}_2\text{Rh}$ (417.18): C, 46.06; H, 4.30; N, 6.71. Found: C, 46.25; H, 4.43; N, 6.89.

2.3d $[\text{Cp}^*\text{IrCl}_2(\text{L}_2)]$ (4): Yellow solid, Yield 92 mg (92%). IR (KBr, cm^{-1}): 3381(s), 3278(s), 3187(m), 2972(w), 1627(s), 1601(w), 1473(s), 1452(s), 1381(m), 1301(w), 1261(w), 1199(w), 1083(w), 1035(m), 782(s), 757(w); ^1H NMR (400 MHz, CDCl_3) δ 8.50 (d, 1H, $H_{\text{HJ}} = 5.25$, py ring), 7.27 (d, 1H, $H_{\text{HJ}} = 4.50$, py ring), 6.53 (t, 1H, py ring), 6.13 (b, 2H, NH_2), 2.11 (s, 3H, CH_3), 1.58 (s, 15H, Cp^* ring); ^{13}C NMR (400 MHz, $\text{DMSO}-d_6 + \text{CDCl}_3$) δ 8.21, 89.65, 99.59, 115.07,

138.13, 156.37; ESI-MS: 507.87 $[\text{M}^+]$ peak; UV-Vis {Acetonitrile, λ_{max} nm ($\epsilon/10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$)}: 228(0.84), 299(0.26). Anal. Calc. for $\text{C}_{16}\text{H}_{23}\text{N}_2\text{Cl}_2\text{Ir}$ (506.49): C, 37.94; H, 4.58; N, 5.53. Found: C, 38.12; H, 4.64; N, 5.70.

2.3e $[\text{Cp}^*\text{RhCl}_2(\text{L}_3)]$ (5): Red orange solid, Yield 80 mg (89%). IR (KBr, cm^{-1}): 3380(s), 3218(s), 3182(m), 3135(s), 2965(w), 2913(m), 1627(s), 1584(m), 1560(m), 1507(m), 1466(w), 1378(w), 1355(m), 1318(s), 1240(s), 1109(s), 1028(m), 891(w), 760(m), 613(s); ^1H NMR (400 MHz, CDCl_3) δ 8.46 (d, 1H, $H_{\text{HJ}} = 4.75$, py ring), 7.20 (d, 1H, $H_{\text{HJ}} = 4.50$, py ring), 6.72 (t, 1H, py ring), 6.31 (b, 2H, NH_2), 1.56 (s, 15H, Cp^* ring); ^{13}C NMR (400 MHz, $\text{DMSO}-d_6 + \text{CDCl}_3$) δ 8.52, 78.22, 98.66, 112.16, 134.47, 155.61; ESI-MS: 449.21 $[\text{M}^+]$ peak; UV-Vis {Acetonitrile, λ_{max} nm ($\epsilon/10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$)}: 262(0.68), 388(0.60). Anal. Calc. for $\text{C}_{15}\text{H}_{20}\text{N}_3\text{Cl}_2\text{O}_2\text{Rh}$ (448.15): C, 40.20; H, 4.50; N, 9.38. Found: C, 40.42; H, 4.66; N, 9.50.

Figure 2. View of H-bonding in metal complexes.

Figure 3. Self-assembly into discrete network architectures of complex **3**; (a) N-H...Cl and CH... π interaction along a axis; (b) CH... π and π ... π interaction along b axis; (c) N-H...Cl and π ... π interactions along c axis; (d) (e) (f) Space filled models representing weak interactions.

2.3f $[Cp^*IrCl_2(L3)]$ (**6**): Yellow solid, Yield 90 mg (82%). IR (KBr, cm^{-1}): 3386(s), 3222(m), 3186(m), 3140(m), 2967(w), 2919(w), 1629(s), 1582(m), 1559(m), 1510(m), 1445(m), 1384(m), 1353(m), 1317(s), 1240(s), 1109(s), 1037(m), 828(w), 758(m), 611(m); 1H NMR (400 MHz, $CDCl_3$) δ 12.12 (s, 1H, CHO), 8.50 (d, 1H, $H_{JJ} = 5.25$, py ring), 7.26 (d, 1H, $H_{JJ} = 4.75$, py ring), 6.96 (t, 1H, py ring), 6.29 (b, 2H, NH_2), 1.58 (s, 15H, Cp^* ring); ^{13}C NMR (400 MHz, $DMSO-d_6 + CDCl_3$) δ 8.18, 77.90, 92.09, 112.20, 134.44, 155.52; ESI-MS: 538.79 $[M^+]$ peak; UV-Vis {Acetonitrile, λ_{max} nm ($\epsilon/10^{-4} M^{-1} cm^{-1}$)}: 259(0.97), 380(0.68). Anal. Calc. for $C_{15}H_{20}N_3Cl_2O_2Ir$ (537.46): C, 33.52; H, 3.75; N, 7.82. Found: C, 33.67; H, 3.86; N, 7.99.

2.3g $[Cp^*RhCl_2(L4)]$ (**7**): Red orange solid, Yield 70 mg (81%). IR (KBr, cm^{-1}): 3360(s), 3242(s), 3212(w), 2965(w), 2917(w), 1664(s), 1613(s), 1562(s), 1456(m), 1381(m), 1259(m), 1197(m), 1124(s), 1026(m), 909(w), 771(s), 673(s), 611(m); 1H NMR (400 MHz, $CDCl_3$) δ 12.12 (s, 1H, CHO), 8.46 (d, 1H, $H_{JJ} = 4.50$, py ring), 7.20 (t, 1H, py ring), 6.95 (d, 1H, $H_{JJ} = 4.75$, py ring), 6.30 (b, 2H, NH_2), 1.58 (s, 15H, Cp^* ring); ^{13}C NMR (400 MHz, $DMSO-d_6 + CDCl_3$) δ 8.52, 78.74, 98.62, 111.92, 144.16, 154.52, 192.91; ESI-MS: 432.25 $[M^+]$ peak; UV-Vis {Acetonitrile, λ_{max} nm ($\epsilon/10^{-4} M^{-1} cm^{-1}$)}: 259(0.77), 349(0.65), 407(0.20). Anal. Calc. for $C_{16}H_{21}N_2Cl_2ORh$ (431.16): C, 44.57; H, 4.91; N, 6.50. Found: C, 44.68; H, 5.06; N, 6.67.

2.3h $[Cp^*IrCl_2(L4)]$ (**8**): Yellow solid, Yield 88 mg (85%). IR (KBr, cm^{-1}): 3362(s), 3255(s), 2967(w), 2918(w), 1667(s), 1614(s), 1565(s), 1453(m), 1404(w), 1381(m), 1258(m), 1196(m), 1123(s), 1034(m), 909(w), 768(m), 674(m), 612(m); 1H NMR (400 MHz, $CDCl_3$) δ

12.17 (s, 1H, CHO), 8.45 (d, 1H, $H_{JJ} = 5.0$, py ring), 7.24 (t, 1H, py ring), 6.98 (d, 1H, $H_{JJ} = 4.75$, py ring), 6.31 (b, 2H, NH_2), 1.56 (s, 15H, Cp^* ring); ^{13}C NMR (400 MHz, $DMSO-d_6 + CDCl_3$) δ 8.32, 78.53, 97.92, 114.64, 145.67, 155.27, 192.71; ESI-MS: 521.91 $[M^+]$ peak; UV-Vis {Acetonitrile, λ_{max} nm ($\epsilon/10^{-4} M^{-1} cm^{-1}$)}: 259(0.41), 346(0.47). Anal. Calc. for $C_{16}H_{21}N_2Cl_2OIr$ (520.47): C, 36.92; H, 4.07; N, 5.38. Found: C, 37.15; H, 4.13; N, 5.45.

3. Results and Discussion

3.1 Synthesis of the complexes

A series of eight new neutral half-sandwich Rh and Ir complexes have been synthesized from the reaction of $[Cp^*M(\mu-Cl)Cl]_2$ ($M = Rh, Ir$) with 1:2 molar equivalents of 2-aminopyridyl ligand (L) in methanol (Scheme 1). These complexes were isolated in very good yield and purified by recrystallization method. All these complexes are red orange/ yellow crystalline solids, resulting as non-hygroscopic, air-stable. They are highly soluble in water and DMSO but they are sparingly soluble in DCM, acetone, acetonitrile and chloroform. All these complexes are fully characterized by IR, 1H & ^{13}C NMR, mass and electronic spectroscopy. Our efforts to make disubstituted mononuclear cationic complexes of type $[Cp^*MCl(L)_2]^+$ with 1:4 molar equivalents of 2-aminopyridyl ligands were unsuccessful.

3.2 Spectral studies of the complexes

IR spectra of metal complexes show bands around at 1625, 1600 cm^{-1} and 1565 cm^{-1} , typical for the

Scheme 1. Syntheses of Cp^*Rh/Cp^*Ir metal compounds.

pyridine skeleton and the out of plane peak at 786 cm^{-1} . 2-aminopyridyl ligands have two nitrogen atoms and both of them can coordinate to the metal ion. When amino nitrogen atom is involved in coordination a strong lower frequency observed in NH_2 stretching vibration ($\Delta = 150\text{--}200\text{ cm}^{-1}$).²² Since there is no shift in NH_2 stretching vibrations, amino nitrogen of 2-aminopyridyl ligands does not involve in coordination in these complexes. The ring breathing mode observed at $983\text{--}898\text{ cm}^{-1}$ for 2-aminopyridyl ligands, is observed at $1025\text{--}1010\text{ cm}^{-1}$ for the complexes. This mode is known to be very sensitive to coordination of pyridine from the ring nitrogen atom and the wave number increases with the strength of the coordination bond. Thus, it is concluded that ring nitrogen is involved in the coordination to the metal in the complexes studied.²³

^1H NMR spectra of all metal complexes, the pyridyl ring protons have shown the signal around $8.5\text{--}6.5$ ppm to corresponding protons and NH_2 group signal shown as broad signal around 6.2 ppm. Complexes **2** and **3** have shown CH_3 protons at 2.1 ppm and complexes **7** and **8** have shown proton of CHO group at 12.1 ppm. The peaks for 2-aminopyridyl ligand protons are observed at higher frequencies in complexes relative to the free ligands, confirming coordination to the Rh/ Ir *via* the pyridine-N atom.²⁴ Moreover all the complexes have displayed a singlet at $\delta\ 1.58$ and $\delta\ 1.53$ ppm due to the Cp^* ligand, which is a slight change in the position of proton signal in comparison to those observed in the starting material of $[\text{Cp}^*\text{MCl}_2]_2$ dimer.²⁵

The ^{13}C NMR spectra of all complexes exhibited five signal in the region at $85.60\text{--}155.90$ ppm for pyridyl ring carbons and sharp single peak at 8.50 ppm that corresponding to Cp^* methyl carbon. The complexes **3**, **4**, **7** and **8** showed single peak at 27.60 ppm and 192.50 ppm for methyl and CHO group carbon of corresponding complexes respectively. These signals are shifted to downfield compared to starting metal precursor and free ligand which indicated the formation of metal complexes.

The mass spectra of all the complexes show their $[\text{M}^+]$ molecular ion peaks as per theoretically expected values and supporting well the formation of complexes. The rhodium complexes display their $[\text{M}^+]$ molecular ion peaks at $m/z\ 404.06, 418.10, 449.21, 432.25$ respectively. The iridium complexes show their $[\text{M}^+]$ molecular ion peaks at $m/z\ 493.72, 507.87, 538.79, 521.91$ respectively.

UV- Visible spectra were recorded in acetonitrile at 10^{-4} M concentration in the range $200\text{--}650$ nm for the all the complexes and shown in figure 4. Spectroscopic

Figure 4. UV- Visible spectra in acetonitrile at 10^{-4} M concentration in the range $200\text{--}650$ nm for the complexes.

data for complexes are presented in table 3. The low spin d^6 - configuration of the mononuclear complexes provides filled orbitals of proper symmetry, which can interact with low lying π^* orbitals of the 2-aminopyridyl ligand. One should therefore expect a band attributable to the MLCT ($t_{2g} - \pi^*$) transition of the electronic spectra, where the transition energy of these bands vary with the nature of the ligands acting as π - acceptors. The presence of an electron donating group (CH_3) in the 2-aminopyridyl ligand decreases of energy of transition, causing red shift in MLCT transition maxima, while an electron withdrawing group (NO_2, CHO) increases the transition energy.²⁶ The UV-visible spectra of all the complexes reveal an intense ligand-localized or intra-ligand $\pi\text{--}\pi^*$ transition in the UV region and a metal to ligand charge transfer (MLCT) $d\pi(\text{M})\text{--}\pi^*(\text{L})$ band in the visible region. All the spectra show a high intense absorption band around $23\text{--}300$ nm, assigned to a $\pi\text{--}\pi^*$ transition, while the less intense absorption band at approximately $360, 390, 405$ nm which are assigned to metal to ligand charge transfers.^{27,28}

Table 3. UV-Vis data of the complexes.

Complexes	$\lambda_{\text{max}}/\text{nm} (\epsilon/10^{-4}\text{ M}^{-1}\text{ cm}^{-1})$		
1	231(0.43)	295(0.12)	401(0.03)
2	231(0.40)	296(0.19)	
3	230(0.74)	297(0.26)	405(0.06)
4	228(0.84)	299(0.26)	
5	262(0.68)	388(0.60)	
6	259(0.97)	380(0.68)	
7	259(0.77)	349(0.65)	407(0.20)
8	259(0.41)	346(0.47)	

3.3 Molecular structural studies

The molecular structures of the mononuclear complexes **3**, **4**, **5**, **6** and **8** have been established by single-crystal X-ray structure analysis. Complexes **3**, **4** and **8** are crystallized in the monoclinic space group $P2_1/c$ and $P21$, and complexes **5** and **6** in the orthorhombic space group $Pbca$. The crystal structure of complex **7** could not be properly solved due to the low number of observed reflections so we have presented only the structure and composition of the molecule. Crystallographic and structure refinement parameters for complexes are shown in table 1 and selected bond distances and bond angles are shown in table 2. The H bonding interactions of metal complexes are shown in table 4. All the complexes display in three-legged piano stool geometry with the metal centre coordinated by the aromatic ligand Cp* and the other three sites to be coordinated by two chloride atoms and monodentate 2-aminopyridyl ligand. The metal atom of all the complexes is in pseudo octahedral arrangement (figure 1).

In the rhodium compounds, the average distance between the metal atom and the C-atoms of the Cp* is 2.153 Å (**3**), 2.148 Å (**5**) and 2.163 Å (**7**). The distance between the Rh atom and the Cp* ring centroid ranges from 1.765 to 1.812 Å while iridium compounds. The average distance between the metal atom and the C-atoms of the Cp* is 2.154 Å (**4**) and 2.146 Å (**8**), and the

distance between the Ir atom and the Cp* ring centroid range around 1.770 Å. These bond distances are almost identical and same as those for other monodentate pyridine-based binuclear Cp*Rh/Cp*Ir complexes.^{29–31}

The average distance of Rh–Cl bond length is 2.427 Å (**3**), 2.413 Å (**5**) and 2.399 Å (**7**) almost identical to the average distance of Ir–Cl bond length is 2.427 Å (**4**) and 2.408 Å (**8**), while Rh–N bond distance is 2.168(2) Å **3**, 2.204(19) Å **5** and 2.248(15) Å **7** shorter than Ir–N bond distance is 2.148(4) Å (**4**) and 2.174(6) Å (**8**). The M–Cl distance does not change significantly but the M–N distance changes drastically depend on the substitution at the 2-aminopyridyl ligand.^{32,33} This could be explained by the difference in electron density at the metal centre caused by the additional of various groups on the 2-aminopyridyl ring. The better donating ability of the methyl substituted 2-aminopyridyl ligand leads to a somewhat weaker M–N interaction in **4** relative to that in **7**. The bond angles of M with ligand and chloride atom are around 87–95° which are normal and close to 90° that is evidence for ‘piano stool’ geometry.

In crystal packing, hydrogen bonding and aromatic-aromatic interactions play important role. In all the complexes, aromatic-aromatic interactions as well as hydrogen bonding are expected to influence crystal packing.^{34,35} We have observed that two different types of hydrogen bonding pattern (intra/inter) in metal complexes depending on the nature of substituent of 2-aminopyridyl components. These hydrogen bonding

Table 4. H- bonding interaction of complexes.

Complex	Donor–H....Acceptor	D–H	H...A	D...A	D–H...A
3	N(2)–H(2)...Cl(2)i	0.86	2.30	3.188	153
	C(6)–H(6B)...Cl(2)ii	0.96	2.72	3.673	173
4	N(2)–H(2)...Cl(2)	0.86	2.35	3.182	162
	C(6)–H(6B)...Cl(2)iii	0.96	2.76	3.696	164
5	N(2)–H(2A)...Cl(2)	0.86	2.37	3.1586	152
	N(2)–H(2B)...O(1)	0.86	2.04	2.6454	127
	N(2)–H(2B)...Cl(1)iv	0.86	2.59	3.2527	135
	C(8)–H(8B)...Cl(2)v	0.96	2.83	3.6209	141
6	N(2)–H(1)...Cl(2)	0.97	2.23	3.142	155
	N(2)–H(2)...O(2)	0.72	2.14	2.645	128
	N(2)–H(2)...Cl(1)vi	0.72	2.69	3.259	138
	C(8)–H(8A)...Cl(2)vii	0.96	2.81	3.669	149
8	N(2)–H(2A)...O(1)	0.86	2.09	2.6984	127
	N(2)–H(2B)...Cl(1)	0.86	2.35	3.1500	155
	C(12)–H(12)...O(1)viii	0.93	2.53	3.3014	140
	C(16)–H(16)...Cl(1)xi	0.93	2.60	3.3927	144

Symmetry transformations used to generate equivalent atoms: i = 1–x, 2–y, –z, ii = x, –1+y, z, iii = x, –1+y, z, iv = 3/2–x, –1/2+y, z, v = 3/2–x, 1/2+y, z, vi = 3/2–x, 1/2+y, z, vii = 3/2–x, –1/2+y, z, viii = 2–x, –1/2+y, 3–z, xi = 1+x, y, 1+z.

distances between N–H–Cl are in the range of 3.142–3.188 Å and distances between N–H–O are in the range of 2.638–2.698 Å (figure 2). The main reason for the discrepancy in hydrogen bonding distance results from the increased acidity (increased donor ability) of the 2-aminopyridyl ligand.^{36–38}

In addition, weak interaction studies reveal the presence of various CH...Cl, CH... π , π ... π interactions in the solid state. Interestingly, in complex **3** it is observed that distances between CH...Cl, CH... π , π ... π are 2.71–2.84, 2.58–2.83 and 3.83–3.84 Å, respectively and result in a grid 2D sheet. Complex **4** shows distances between CH...Cl, π ... π as 2.71–2.84, 3.83–3.84 Å, respectively and result in a grid 2D sheet but without CH... π interaction. These interactions may be called van der Waals interactions, since the lengths are significantly less than the sum of the van der Waals radii (2.8 and 3.1 Å, respectively).³⁹ (figure 3).

4. Conclusion

In summary, Cp*Rh and Cp*Ir complexes containing with 2-aminopyridyl ligand have been synthesized successfully. All these complexes are fully characterized by spectroscopic methods and confirmed by XRD techniques. X-ray analyses established the coordination of nitrogen atoms to the metal centres as monodentate ligand. Moreover, all the metal complexes containing 2-aminopyridine were found to form inter/intramolecular hydrogen bonds such as N–H–Cl and also CH...Cl, CH... π , and π ... π interactions.

Supplementary Information

CCDC numbers 1018330 (**3**), 101831 (**4**), 1018332 (**5**), 1018333 (**6**), 1018334 (**7**), 1018335 (**8**) contain the supplementary crystallographic data for the compounds. 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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