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Synthesis and structural studies of half-sandwich Cp* rhodium and Cp* iridium complexes featuring mono, bi and tetradentate nitrogen and oxygen donor ligands

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Abstract. A series of Cp*Rh and Cp*Ir complexes of various nitrogen and oxygen donor ligands were synthesized and characterized. Mono, bi and tetradentate ligands were used to synthesize mononuclear and dinuclear complexes. Schiff base derivatives of picolinic hydrazine and 5-aminoquinoline were used in the synthesis of complexes **1–8**. Among the ligands used for complexation, **L1** and **L2** act as bidentate, **L3** as monodentate and **L4** as tetradentate in forming the corresponding complexes. All the complexes were characterized by spectroscopic techniques and the structures of complexes **2**, **3**, **5** and **7** were unambiguously characterized by single crystal X-ray crystallography. Complexes **2** and **7** were found to have π - π stacking interactions and solvent to complex interactions, respectively. Metal-mediated deprotonation of N-H and monodentate binding of nitrogen are attributed to the formation of neutral complexes whereas ionic complexes are formed by (N,O) bonding.

Keywords. Picolinic hydrazine; fluorene 2-carbaldehyde; rhodium; iridium.

1. Introduction

In the field of organometallic chemistry, Cp*Rh and Cp*Ir complexes have occupied a significant position with their readiness to form stable complexes with a variety of ligands. They are found as good catalysts in water oxidation,^{1,2} hydrogen activation,³ dehydrogenation,⁴ transfer (de)hydrogenation⁵ and aerobic alcohol oxidation.⁶ Cp* rhodium complexes containing *ortho* or *meta*-phenyl-bridged pyridinium ligands catalyze the transfer of hydrogenation of imines by mimicking biological enzymes.⁷ Though there is a limited number of reports on the anticancer activity of rhodium and iridium complexes compared to that of ruthenium, the interest in screening their potency is gaining momentum and those showing good antitumor activities which have drawn the attention of organometallic chemists.^{8–12} In our group, we have synthesized numerous complexes of Cp* rhodium and Cp* iridium with various chelating nitrogen donor ligands *viz.*, pyridyl pyrazines, pyridyl diketone, 3,5-bis(2-pyridyl)pyrazole, 2-substituted-1,8-naphthyridine, pyridyl thioether ligand and oxygen donor ligands.^{13–16} Neutral complexes of Cp* rhodium and iridium-containing chelating nitrogen

donor picolinamide derivatives, where one of the two nitrogens is anionic were found to exhibit significant cytotoxicity on HT-29, MCF-7, A2780 and cisplatin-resistant A2780cis cancer cell lines.^{17,18}

Acylhydrazones, in particular, the Schiff base derivatives of picolinic hydrazine are versatile nitrogen and oxygen donor ligands with biological applications such as iron chelators, antibacterial and fluorescence sensing agents.^{19–21} Acylhydrazones are exploited as widely tunable photoswitches.²² Various metal complexes of hydrazine-derived ligands have been reported with fascinating functionalities and bonding modes, potential catalysts, biologically active agents and single molecule magnets.^{23–28} In acylhydrazone ligands, deprotonation of the –NH group is readily achieved, mediated by base or metal while forming complexes and is responsible for various serendipitous bonding modes.²⁹ Among all the complexes which we report here, metal-mediated deprotonation of –NH group is observed because it is achieved even without using any base.

In the present study, we have synthesized and characterized Cp* rhodium and Cp* iridium complexes of various Schiff bases derived from picolinic hydrazine and 5-aminoquinoline and their bonding modes were elucidated by crystallographic studies.

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2. Experimental

2.1 Materials and physical measurements

All the reactions were performed under an ambient atmosphere without using either nitrogen or an inert gas such as argon. Metal chlorides $\text{MCl}_3 \cdot x\text{H}_2\text{O}$ ($\text{M} = \text{Rh}$ and Ir) were purchased from Arora Matthey Limited, India. Pentamethylcyclopentadiene (Sigma-Aldrich, India), hydrazine hydrate (SD fine, India), methyl picolinate (Sigma-Aldrich, India), 2-benzoyl acetone (Sigma-Aldrich, India), 4-cyanobenzaldehyde (Spectrochem, India) were used as received. All the solvents used for the synthesis were dried and distilled prior to use according to the standard procedures and stored over activated molecular sieves.³⁰ Picolinic hydrazine was prepared by modifying the literature method and ligands (**L1–L4**) were prepared by Schiff base condensation method.³¹ Precursor compounds viz., $[\{\text{Cp}^*\text{RhCl}_2\}_2]$ and $[\{\text{Cp}^*\text{IrCl}_2\}_2]$ were prepared according to the literature methods.³² Elemental analyses were performed on a Perkin-Elmer-2400 CHN analyser. Infrared (IR) spectra were recorded on a Perkin-Elmer 983 spectrophotometer for compounds dispersed in KBr discs. ^1H NMR spectra were recorded with Bruker Avance II 400 MHz spectrometer. Chemical shifts for ^1H NMR are reported using tetramethylsilane (TMS) as the internal standard. UV-Vis spectra were recorded by using Perkin-Elmer Lambda 25 Spectrophotometer. ESI mass spectra were recorded on Bruker micro TOF-Q II spectrometer. Single crystals picked up from the samples were analyzed on Oxford Diffraction Xcalibur Eos Gemini diffractometer using $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) in the whole reciprocal sphere.³³ All the structures were solved by direct methods with SHELXS-97³⁴ and the molecular model refined by full-matrix least squares procedure on F^2 with SHELXL-97.³⁵ All the non-hydrogen atoms were refined anisotropically while hydrogen atoms were placed in geometrically ideal positions and constrained to ride on their parent atoms. The molecular structures presented as ORTEP were drawn with ORTEP-3 graphical software.³⁶ The packing diagrams in Figures 5, 7 and 10 were drawn using Mercury 3.6 programme.³⁷

2.2 Synthesis of ligands L1–L4

2.2a Ligand L1: Picolinic hydrazine (200 mg, 1.45 mmol) and 1-Phenylbutane-1,3-dione (283 mg, 1.75 mmol) were refluxed in methanol (20 mL) for six hours with two drops of glacial acetic acid. The resulting yellow solution was rotary-evaporated and the yellow solid obtained was washed with diethyl ether and air-dried. Yield: 270 mg (66%). M.p.: 104–107°C. FTIR [KBr, cm^{-1}]: 3341 (s) $\nu(\text{N-H})$, 1700 $\nu(\text{C=O})$, 1596 (s) $\nu(\text{C=N})$. ^1H NMR (δ , ppm in CDCl_3): 10.83 (s, 1H, N-H), 8.51 (t, 1H, py), 8.27 (d, 1H, py), 8.16 (d, 2H, Ph), 7.81 (d, 2H, Ph), 7.52 (t, 1H, py), 7.43 (m, 1H, Ph), 4.15 (s, 2H, CH_2), 2.15 (s, 3H, Me). UV-vis (MeOH): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{L mol}^{-1} \text{ cm}^{-1}$): 263 (2.40×10^4), 337 (1.35×10^4), 422 (1.47×10^4). Anal. Calcd. (%) For $\text{C}_{16}\text{H}_{15}\text{N}_3$

O_2 : C, 68.31; H, 5.37; N, 14.94. Found (%): C, 68.48; H, 5.58; N, 15.14. ESI MS (m/z): calcd: 281.1164; found: 281.1150.

2.2b Ligand L2: Picolinic hydrazine (200 mg, 1.45 mmol) and fluorine 2-carbaldehyde (281 mg, 1.45 mmol) were refluxed in methanol (20 mL) for six hours with two drops of glacial acetic acid. The resulting pale yellow solution was rotary-evaporated and the pale yellow crystalline solid obtained was washed with diethyl ether and air-dried. Yield: 364 mg (80%). M.p.: 206–210°C. FTIR [KBr, cm^{-1}]: 3275 (s) $\nu(\text{N-H})$, 1673 $\nu(\text{C=O})$, 1523 (s) $\nu(\text{C=N})$. ^1H NMR (δ , ppm in CDCl_3): 10.93 (s, 1H, N-H), 8.52 (d, 1H, py), 8.27 (d, 1H, py), 8.05 (s, 1H, $=\text{C-H}$), 7.84 (t, 1H, py), 7.74 (t, 1H, py), 7.69 (d, 1H, Ph), 7.50 (d, 1H, Ph), 7.43 (t, 1H, Ph), 7.31 (m, 2H, Ph), 3.87 (s, 2H, CH_2). UV-vis (MeOH): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{L mol}^{-1} \text{ cm}^{-1}$): 227 (3.79×10^4), 265 (2.86×10^4), 339 (8.26×10^4). Anal. Calcd. (%) for $\text{C}_{20}\text{H}_{15}\text{N}_3\text{O}$: C, 76.66; H, 4.82; N, 13.41. Found (%): C, 76.86; H, 4.98; N, 13.65%. ESI MS (m/z): calcd: 313.1215; Found: 313.1200.

2.2c Ligand L3: 5-Amino quinoline (144 mg, 1 mmol) and fluorine 2-carbaldehyde (194 mg, 1 mmol) were refluxed in methanol (20 mL) with two drops of glacial acetic acid for six hours. The resulting yellow solution was rotary-evaporated and the yellow solid obtained was washed with diethyl ether and air-dried. Yield: 250 mg (78%). M.p.: 182°C. FTIR [KBr, cm^{-1}]: 3060 (m) $\nu(\text{C-H})$, 2931 (m) $\nu(\text{C-H})$, 1619 (s) $\nu(\text{C=N})$, 1606 (s) $\nu(\text{C=C})$. ^1H NMR (δ , ppm in CDCl_3): 8.71 (d, 1H, py), 8.56 (s, 1H, Ph), 8.18 (s, 1H, $=\text{C-H}$), 7.90 (t, 1H, py), 7.81 (m, 2H, Ph), 7.64 (t, 1H, py), 7.53 (d, 1H, Ph), 7.36 (m, 2H, Ph), 7.14 (d, 1H, py), 3.94 (s, 2H, CH_2). UV-vis (MeOH): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{L mol}^{-1} \text{ cm}^{-1}$): 274 (8.68×10^4), 316 (5.31×10^4). Anal. Calcd. (%) for $\text{C}_{23}\text{H}_{16}\text{N}_2$: C, 86.22; H, 5.03; N, 8.74. Found (%): C, 86.40; H, 5.20; N, 8.90. ESI MS (m/z): calcd: 320.1313; Found: 320.1285.

2.2d Ligand L4: Picolinic hydrazine (200 mg, 1.45 mmol) and 4-cyanobenzaldehyde (190 mg, 1.45 mmol) were refluxed in methanol with two drops of glacial acetic acid for six hours. The resulting white crystalline solid obtained was washed with diethyl ether and air-dried. Yield: 255 mg (72%). M.p.: 256°C. FTIR [KBr, cm^{-1}]: 3302 (s) $\nu(\text{N-H})$, 2227 (s) $\nu(\text{C=N})$, 1690 (s) $\nu(\text{C=O})$, 1589 (s) $\nu(\text{C=N})$. ^1H NMR (δ , ppm in CDCl_3): 11.51 (s, 1H, N-H), 8.33 (d, 1H, py), 8.28 (s, 1H, $=\text{C-H}$), 7.94 (d, 1H, py), 7.62 (d, 2H, Ph), 7.39 (d, 2H, py), 7.24 (t, 1H, py). UV-vis (MeOH): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{L mol}^{-1} \text{ cm}^{-1}$): 240 (6.55×10^4), 273 (6.11×10^4), 348 (3.69×10^4). Anal. Calcd. (%) for $\text{C}_{14}\text{H}_{10}\text{N}_4\text{O}$: C, 67.19; H, 4.03; N, 22.39. Found (%): C, 66.89; H, 4.23; N, 22.69%. ESI-MS (m/z): calc: 250.0855; Found: 250.0905.

2.3 Synthesis of complexes 1–8

Complexes **1–6** were prepared by the procedure as follows: A mixture of the precursor compound $[\{\text{Cp}^*\text{RhCl}_2\}_2]$ (50 mg, 0.08 mmol), ligands **L1–L3** (0.16 mmol) for complexes **1**,

Figure 1. Ligands used in this study.

Scheme 1. Schematic presentation of the synthesis of complexes 1–8.

3, 5, and $[\text{Cp}^*\text{IrCl}_2]_2$ (50 mg, 0.06 mmol), ligands **L1–L3** (0.12 mmol) for complexes **2, 4, 6** were dissolved in methanol (10 mL) and stirred for six hours. The yellow color solution was rotary-evaporated and the residue was dissolved in dichloromethane and filtered through celite. The concentrated solution of the compound was precipitated with diethylether (15 mL) and washed with the same solvent for a couple of times (2×10 mL) and air-dried.

2.3a $[\text{Cp}^*\text{RhL1}\kappa^2_{(N\cap N)}\text{Cl}]$ (**1**): Yield: 41 mg (47%). FTIR [KBr, cm^{-1}]: 2925 (m) $\nu_{(\text{C-H})}$, 1640 $\nu_{(\text{C=O})}$, 1590 (s) $\nu_{(\text{C=N})}$. ^1H NMR (δ , ppm in CDCl_3): 8.62 (t, 1H, py), 8.35 (d, 1H, py), 8.26 (d, 2H, Ph), 7.91 (d, 2H, Ph), 7.60 (t, 1H, py), 7.52 (m, 1H, Ph), 4.26 (s, 2H, CH_2), 2.24 (s, 3H, Me), 1.65 (s, 15H, Cp^*). UV-Vis (MeOH): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{L mol}^{-1}$):

269 (2.58×10^4). ESI-MS m/z : 518.1032 $[\text{M}-\text{Cl}]$.

2.3b $[\text{Cp}^*\text{IrL1}\kappa^2_{(N\cap N)}\text{Cl}]$ (**2**): Yield: 45 mg (58%). FTIR [KBr, cm^{-1}]: 2920 (m) $\nu_{(\text{C-H})}$, 1645 $\nu_{(\text{C=O})}$, 1592 (s) $\nu_{(\text{C=N})}$. ^1H NMR (δ , ppm in CDCl_3): 8.70 (t, 1H, py), 8.45 (d, 1H, py), 8.28 (d, 2H, Ph), 7.98 (d, 2H, Ph), 7.70 (t, 1H, py), 7.62 (m, 1H, Ph), 4.36 (s, 2H, CH_2), 2.25 (s, 3H, Me), 1.70 (s, 15H, Cp^*). UV-Vis (MeOH): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{L mol}^{-1}$): 268 (8.84×10^4), 373 (0.97×10^4). ESI-MS m/z : 608.1971 $[\text{M}-\text{Cl}]$. Single crystals suitable for XRD were obtained by solvent diffusion method by diffusing diethyl ether into a saturated methanolic solution of the complex.

2.3c [$Cp^*RhL2\kappa^2_{(N\cap N)}Cl$] (**3**): Yield: 59 mg (64%). FTIR [KBr, cm^{-1}]: 2921 (m) $\nu(C-H)$, 1620(s) $\nu(C=O)$, 1590 (s) $\nu(C=N)$, 1556 (s) $\nu(C=C)$. 1H NMR (δ , ppm in $CDCl_3$): 9.1 (s, 1H, $=C-H$), 8.77 (d, 1H, py), 8.32 (t, 1H, py), 8.04 (d, 1H, py), 7.91 (m, 2H, py), 7.80 (d, 1H, Ph), 7.59 (t, 1H, Ph), 7.40 (t, 1H, Ph), 7.30 (t, 1H, Ph), 3.90 (s, 2H, CH_2), 1.67 (s, 30H, Cp^*). UV-Vis (MeOH): λ_{max}/nm ($\epsilon/L mol^{-1} cm^{-1}$): 269 (5.0×10^4), 386 (0.97×10^4). ESI-MS m/z : 550.1410 [M-Cl]. Single crystals suitable for XRD were obtained by solvent diffusion method by diffusing hexane into a saturated chloroform solution of the complex.

2.3d [$Cp^*IrL2\kappa^2_{(N\cap N)}Cl$] (**4**): Yield: 60 mg (74%). FTIR [KBr, cm^{-1}]: 2922 (m) $\nu(C-H)$, 1625 (s) $\nu(C=O)$, 1595 (s) $\nu(C=N)$, 1556 (s) $\nu(C=C)$. 1H NMR (δ , ppm in $CDCl_3$): 8.88 (s, 1H, $=C-H$), 8.57 (d, 1H, py), 8.21 (t, 1H, py), 7.94 (d, 1H, py), 7.81 (m, 2H, Ph), 7.56 (d, 1H, Ph), 7.49 (t, 1H, py), 7.39 (t, 1H, Ph), 7.33 (t, 1H, Ph), 3.95 (s, 2H, CH_2), 1.66 (s, 30H, Cp^*). UV-vis (MeOH): λ_{max}/nm ($\epsilon/L mol^{-1} cm^{-1}$): 240 (8.29×10^4), 353 (4.34×10^4). ESI-MS m/z : 640.1940 [M-Cl].

2.3e [$Cp^*RhL3_{(N)}$] (**5**): Yield: 62 mg (63%). FTIR [KBr, cm^{-1}]: 2912 (m) $\nu(C-H)$, 1623 (s) $\nu(C=N)$, 1605 (s) $\nu(C=C)$. 1H NMR (δ , ppm in $CDCl_3$): 9.02 (s, 1H, $=C-H$), 8.83 (t, 1H, py), 8.72 (d, 1H, py), 8.25 (d, 1H, py), 8.01 (d, 1H, py), 7.98 (d, 1H, py), 8.02 (t, 1H, py), 7.77 (d, 1H, py), 7.65 (t, 1H, py), 7.48 (m, 2H, Ph), 7.25 (t, 2H, Ph), 3.9 (s, 2H, CH_2), 1.62 (s, 15H, Cp^*). UV-Vis (MeOH): λ_{max}/nm ($\epsilon/L mol^{-1} cm^{-1}$): 270 (5.40×10^4). ESI-MS m/z : 558.1540 [M-Cl₂]. Single crystals suitable for XRD were obtained by solvent diffusion method by diffusing hexane into a saturated chloroform solution of the complex.

2.3f [$Cp^*IrL3_{(N)}Cl$] (**6**): Yield: 65 mg (80%). FTIR [KBr, cm^{-1}]: 2912 (m) $\nu(C-H)$, 1625 (s) $\nu(C=N)$, 1595 (s) $\nu(C=C)$. 1H NMR (δ , ppm in $CDCl_3$): 8.80 (s, 1H, $=C-H$), 8.73 (t, 1H, py), 8.61 (d, 1H, py), 8.20 (d, 1H, py), 7.94 (d, 1H, py), 7.88 (d, 1H, py), 7.82 (t, 1H, py), 7.67 (d, 1H, py), 7.56 (t, 1H, py), 7.38 (m, 2H, Ph), 7.15 (t, 1H, py), 3.95 (s, 2H, CH_2), 1.69 (s, 15H, Cp^*). UV-Vis (MeOH): λ_{max}/nm ($\epsilon/L mol^{-1} cm^{-1}$): 239 (4.30×10^4), 352 (2.69×10^4). ESI-MS m/z : 648.2120 [M-Cl₂].

2.3g [$(Cp^*RhCl)_2L4_{\{\kappa^2_{(N\cap N)}-\kappa^2_{(N\cap O)}\}}PF_6$] (**7**): A mixture of precursor compound [Cp^*RhCl_2] (50 mg, 0.08 mmol), ligand **L4** (40 mg, 0.16 mmol) and NH_4PF_6 (0.2 mmol) were dissolved in methanol (10 mL) and stirred for six hours. The yellow color precipitate formed during the course of the reaction was washed with diethyl ether (2×15 mL) and air-dried. Single crystals suitable for XRD were obtained by solvent diffusion method by diffusing hexane into a saturated dichloromethane solution of the complex. Yield: 45 mg (60%). FTIR [KBr, cm^{-1}]: 2925 (m) $\nu(C-H)$, 2234 (s) $\nu(C\equiv N)$, 1609 (m) $\nu(C=O)$, 1573 (s) $\nu(C=N)$, 1573 (s) $\nu(C=C)$, 844 (vs) $\nu(P-F)_{str}$, 558

Figure 2. UV-Vis spectra of ligands L1-L4.

Figure 3. UV-Vis spectra of complexes 1-8.

(s) $\nu(P-F)_{ben}$. 1H NMR (δ , ppm in $CDCl_3$ and acetone- d_6): 9.35 (s, 1H, $=C-H$), 8.66 (d, 1H, py), 8.54 (t, 1H, py), 8.33 (d, 1H, py), 8.21 (d, 2H, Ph), 8.12 (t, 1H, py), 7.82 (d, 2H, Ph), 1.38 (s, 15H, Cp^*), 1.28 (s, 15H, Cp^*). UV-Vis (MeOH): λ_{max}/nm ($\epsilon/L mol^{-1} cm^{-1}$): 242 (5.0×10^4), 386 (1.66×10^4). ESI-MS m/z : 795.0670 [M- PF_6], 487.1016 [M- PF_6 - Cp^*RhCl_2].

2.3h [$(Cp^*IrCl)_2L4_{\{\kappa^2_{(N\cap N)}-\kappa^2_{(N\cap O)}\}}PF_6$] (**8**): Complex **8** was prepared similar to complex **7** by using [Cp^*IrCl_2] (30 mg, 0.12 mmol), ligand **L4** (50 mg, 0.12 mmol) and NH_4PF_6 (0.2 mmol). Yield: 48 mg (70%). FTIR [KBr, cm^{-1}]: 2925 (m) $\nu(C-H)$, 2228 (s) $\nu(C\equiv N)$, 1626 (m) $\nu(C=O)$, 1598 (s) $\nu(C=N)$, 1564 (s) $\nu(C=C)$, 846 (vs) $\nu(P-F)_{str}$, 558 (s) $\nu(P-F)_{ben}$. 1H NMR (δ , ppm in $CDCl_3$ and acetone- d_6): 9.41 (s, 1H, $=C-H$), 8.87 (d, 1H, py), 8.50 (d, 1H, py), 8.37 (d, 2H, Ph), 8.24 (t, 1H, py), 8.00 (t, 1H, py), 7.90 (d, 2H, Ph), 1.53 (s, 15H, Cp^*), 1.37 (s, 15H, Cp^*). UV-Vis (MeOH): λ_{max}/nm ($\epsilon/L mol^{-1} cm^{-1}$): 243 (5.03×10^4), 389 (0.82×10^4). ESI-MS m/z : 973.1740 [M- PF_6], 577.158 [M- PF_6 - Cp^*IrCl_2].

Table 1. Crystallographic and structure refinement parameters for complexes **2**, **3**, **5** and **7**.

	2	3	5	7[PF₆]
Empirical formula	C ₂₇ H ₃₃ ClIrN ₃ O ₃	C ₃₀ H ₂₉ ClN ₃ ORh	C _{27.20} H ₂₄ C ₁₄ N _{1.60} Rh _{0.80}	C ₃₅ H ₄₁ C ₁₄ F ₆ N ₄ OPRh ₂
Formula weight	675.21	585.92	599.05	1026.31
Temperature (K)	293(2)	293(2)	293(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>Pca</i> 21	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions (Å, °)				
a	10.647(2)	16.9838(9)	7.5644(4)	8.3490(5)
b	11.562(2)	7.9705(6)	22.2101(9)	29.5901(12)
c	11.666(2)	38.6554(18)	21.1554(11)	16.8571(7)
α	79.59(3)	90	90.00	90.00
β	84.08(3)	90	92.497(4)	97.391(4)
γ	68.05(3)	90	90.00	90.00
Volume (Å ³ , Z)	1309.1(4), 2	5232.7(5), 8	3550.9(3), 5	4129.9(3), 4
Calculated density (mg m ⁻³)	1.713	1.487	0.882	1.651
Absorption coefficient (mm ⁻¹)	5.235	0.783	1.400	1.157
Crystal size (mm ³)	0.14 × 0.12 × 0.11	0.48 × 0.13 × 0.04	0.21 × 0.18 × 0.17	0.09 × 0.05 × 0.05
Scan range	1.78 to 24.89	3.013 to 28.71	3.033 to 26.371	3.01 to 28.77
Reflections collected	4542	9163	3780	9453
Independent reflections (R _{int})	4119 (0.1011)	7525 (0.0464)	3780 (0.0712)	5965 (0.0601)
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data/restraints/parameters	4542/0/308	7525/1604/603	3780/0/382	5965/24/558
Goodness-of-fit on F ²	1.107	1.104	1.7636	1.034
Final R indices [I > 2σ(I)]*	R1 = 0.0481, wR2 = 0.0529	R1 = 0.0628, wR2 = 0.0808	R1 = 0.0634, wR2 = 0.1414	R1 = 0.0557, wR2 = 0.1089
R indices (all data)	R1 = 0.1258, wR2 = 0.1278	R1 = 0.1217, wR2 = 0.1304	R1 = 0.063, wR2 = 0.978	R1 = 0.0824, wR2 = 0.0989
Largest difference peak and hole (e Å ⁻³)	4.653 and -1.800	0.852 and -1.289	4.1522 and -1.3750	0.547 and -0.559

*Structures were refined on F_0^2 : $wR2 = [\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma w(F_0^2)^2]^{1/2}$, where $w^{-1} = [\Sigma(F_0^2) + (aP)^2 + bP]$ and $P = [\max(F_0^2, 0) + 2F_c^2]/3$.

Table 2. Selected bond lengths and bond angles of complexes **2**, **3**, **5** and **7**.

	2	3	5	7
Rh1/Ir1-Cp* _{cent}	1.785	1.795	1.791	1.766
Rh2/Ir2-Cp* _{cent}				1.795
Rh1/Ir1-Cp* _{avg}	2.158	2.162	2.145	2.141
Rh2/Ir2-Cp* _{avg}				2.161
Rh1/Ir1-N1	2.097(6)	2.094(8)	2.186(4)	2.095(4)
Rh1/Ir1-N2	2.083(6)	2.100(7)		2.132(3)
Rh1/Ir1-Cl1	2.419(2)	2.428(3)	2.4155(17)	2.398(13)
Rh1/Ir1-Cl2			2.4204(17)	2.397(13)
C16-O1	1.241(10)	1.231(11)		1.259(5)
C16-N2	1.335(10)	1.341(12)		1.330(5)
N2-N3	1.393(9)	1.383(11)		1.402(5)
N2-Rh1/Ir1-N1	75.6(2)	75.9(3)		76.07(14)
N1-Rh1/Ir1-Cl1	82.42(19)	89.1(2)	92.7(3)	89.24(11)
N2-Rh1/Ir1-Cl1	87.76(19)	91.8(2)		88.23(10)
N2-Rh1/Ir1-Cl2			87.9(3)	
Cl-Rh1/Ir1-Cl2			88.85(6)	
Rh2/Ir2-N3				2.159(4)
Rh2/Ir2-O1				2.113(3)
Rh2/Ir2-Cl2				2.398(13)
O1-Rh2/Ir2-N3				75.79(12)
O1-Rh2/Ir2-Cl2				84.88(9)
N3-Rh2/Ir2-Cl2				90.44(10)
N1-C15-C16-N2	3.98	6.87		0.90
N3-N2-C16-O1			–	10.99
C16-N3-N2-C17	78.85			

3. Results and Discussion

3.1 Synthesis of complexes

Schiff base ligands derived from picolinic hydrazine and 5-aminoquinoline with carbonyl compounds (**L1–L4**) (Figure 1) were prepared by condensation in the presence of acetic acid.

The reaction of Cp* rhodium and Cp* iridium precursor complexes with ligands **L1–L4** have yielded complexes **1–8** (Scheme 1). All the complexes were obtained as yellow powder. The ligands **L1** and **L2** are bidentate, **L3** is monodentate and **L4** is tetradentate while forming complexes. All the complexes are soluble in polar solvents such as dichloromethane, chloroform, acetone, methanol and acetonitrile but insoluble in nonpolar solvents such as hexane, diethyl ether and petroleum ether. Complexes **1–6** are neutral whereas **7** and **8** are cationic with hexafluorophosphate counterion. Deprotonation of the N-H proton during the course of the reaction attributes for the formation of neutral complexes **1–4**, complexes **5** and **6** are neutral by virtue of the monodentate bound ligand.

3.2 Characterization by spectral studies

3.2a IR and NMR spectral studies: The changes in the functional groups such as carbonyl, amine and PF₆ are observed from IR spectra. In ligands **L1**, **L2** and **L4**, the carbonyl stretching frequencies are observed at 1673–1700 cm^{–1} which are found to decrease in complexes after binding to metal. Similarly, in complexes **1–4**, **7** and **8**, it is observed at 1609–1645 cm^{–1}. Ligands **L1**, **L2** and **L4** exhibited a sharp band at 3302–3341 cm^{–1} for N-H which has disappeared in the corresponding complexes viz., **1–4**, **7** and **8** due to its deprotonation by the metal. In ligand **L4** and its corresponding complexes, **7** and **8**, stretching frequency of cyanide is observed at 2227, 2234 and 2228 cm^{–1}, respectively, where an increase is observed in complexes compared to that of the ligand. The ionic nature of complexes **7** and **8** with PF₆ counter ion is supported by the stretching frequency of P-F at 844 and 846 cm^{–1}, respectively and bending frequency at 558 cm^{–1} for the both. ¹H NMR spectral studies have supported the deprotonation of the N-H proton upon binding to the metal by the absence of the singlet of the N-H in the corresponding complexes.³⁸ In

Figure 4. The molecular structure of complex **2** depicted as ORTEP with 50% thermal ellipsoid probability level. Hydrogen atoms are omitted for clarity.

Figure 5. The H-Cl, O-H, π - π interactions in complex **2**.

ligands **L1**, **L2** and **L4**, it is observed at 10.83, 10.93 and 11.51 ppm, respectively. The presence of arene metal portion is confirmed by the singlet resonances of fifteen protons, each of Cp* ring at 1.65–1.71 ppm in complexes **1–6**. In complex **7**, the two Cp* rings are observed at 1.38 and 1.28 ppm and in complex **8** they

are observed at 1.53 and 1.37 ppm, respectively, which shows a deshielding in the latter and also supports the dinuclear complexes.³⁹ In ligands **L2** and **L3**, the methylene (CH₂) of fluorine 2-carbaldehyde is observed at 3.87 and 3.94 ppm respectively and in complexes **5** and **6** corresponding to **L2** and **L3**, it is observed at 3.90 and 3.95 ppm, respectively. The aldimine proton in ligands **L2**, **L3** and **L4** resonated as a singlet at 8.05, 8.18 and 8.28 ppm, respectively. In the corresponding complexes **3–8**, it is downfield shifted significantly which is at 9.1 and 8.88 ppm in complexes **3** and **4** (complexes from **L2**), 9.02 and 8.80 ppm in complexes **5** and **6** (complexes from **L3**), 9.35 and 9.41 ppm in complexes **7** and **8** (complexes from **L4**). It illustrates the greater electron withdrawing nature of cyanobenzene than that of fluorine where the former causes more deshielding of the C-H proton. From the mass spectral study, we found that in mononuclear complexes **1–6**, [M-Cl] ion is the molecular ion peak. In dinuclear complexes **7** and **8**, the [M-PF₆] is the molecular ion peak and the base peak is the mononuclear complex without chlorides.

Figure 6. The molecular structure of complex **3** depicted as ORTEP with 50% thermal ellipsoids probability level. Hydrogen atoms are omitted for clarity.

3.2b UV-visible spectral study: UV-Vis spectra of the ligands **L1–L4** and complexes **1–8** were recorded in methanol at 10 μM at room temperature. Electronic spectra of ligands and all the complexes are depicted in Figures 2 and 3. The ligands exhibited medium intensity bands at $\sim 220\text{--}240\text{ nm}$ and high-intensity bands at $263\text{--}274\text{ nm}$ and $316\text{--}348\text{ nm}$. Ligand **L1** exhibited a high-intensity band in the visible region at 422 nm . In complexes **1–4** a high-intensity band is observed at $\sim 270\text{ nm}$ and in complexes **5–8** it is observed at $\sim 240\text{ nm}$. There is a bathochromic shift from $\sim 340\text{ nm}$ to $\sim 370\text{--}390\text{ nm}$ in complexes **1–6**. The high energy bands around 240 nm correspond to $\pi\text{--}\pi^*$ transitions which include intra-ligand charge transfer transitions (ILCT), the transitions around $\sim 370\text{--}390\text{ nm}$ correspond to $n\text{--}\pi^*$ transitions and can be assigned to metal to ligand charge transfer transitions (MLCT).⁴⁰

3.2c Structural studies by X-ray crystallography: The molecular structures of complexes **2**, **3**, **5** and **7** have been elucidated by single-crystal X-ray structure analysis.

Figure 7. The H-Cl and O-H interactions in complex **3**.

Figure 8. The molecular structure of complex **5** depicted as ORTEP with 50% thermal ellipsoid probability level. Hydrogen atoms are omitted for clarity.

Crystallographic data and structure refinement parameters of the complexes **2**, **3**, **5** and **7**, and their selected bond lengths and bond angles are given in Tables 1 and 2, respectively.

In complex **2**, the centroid is located at 1.785 Å from iridium. The Ir(1)-N(1), Ir(1)-N(2) and Ir(1)-Cl(1) bond distances are $2.097(6)\text{ Å}$, $2.083(6)\text{ Å}$ and $2.419(2)\text{ Å}$, respectively. The bond distances of C(16)-O(1) and C(20)-O(2) are $1.241(10)\text{ Å}$ and $1.247(10)\text{ Å}$, respectively, supporting the keto form. The bite angles around the metal range from $75.60(2)^\circ$ to $87.76(19)^\circ$ suggesting the pseudo-octahedral geometry. The torsional angle around N(1)-C(15)-C(16)-N(2) is 3.98° . The torsion angle at C(16)-N(3)-N(2)-C(17) is 78.85° which suggests the perpendicular alignment of the picolinic hydrazine and the benzoyl pyridine moieties (Figure 4). In complex **2**, $\pi\text{--}\pi$ stacking interactions are found between two Cp* rings at 3.628 Å . The H-Cl interaction is found between the metal chloride and the hydrogen of the methanol at 2.49 Å (H1S-Cl1). The O-H interaction is observed between the carbonyl oxygen and hydrogen of Cp* at 2.55 Å (O2-H6B) (Figure 5).

In complex **3**, Rh is located from the Cp* at 1.795 Å and two nitrogen atoms N1 and N2 at $2.094(8)\text{ Å}$ and $2.100(7)\text{ Å}$ and chloride at $2.428(3)\text{ Å}$. The keto nature of the C(16)-O(1) is supported by the bond length $1.231(11)\text{ Å}$. The bite angles around the metal range from $75.90(3)^\circ$ to $91.80(2)^\circ$, respectively, suggest the pseudo-octahedral arrangement (Figure 6).

In complex **3**, intermolecular O-H and H-Cl interactions were found. The H-Cl interaction was found between the metal chloride and Cp* methyl hydrogen at 2.838 Å and O-H interaction was found between carbonyl oxygen and Cp* methyl hydrogen at 2.570 Å (Figure 7).

In complex **5**, the rhodium metal is located at 1.791 Å from the centroid and $2.186(4)\text{ Å}$ from the nitrogen

Figure 9. The molecular structure of complex **7** depicted as ORTEP with 50% thermal ellipsoid probability level. Hydrogen atoms are omitted for clarity.

Figure 10. The N-H, O-H, H-Cl interactions between solvent and complex in complex **7**.

(N1), 2.415(17) and 2.420(17) Å, respectively, from the two chlorides Cl(1) and Cl(2).

The bite angles around metal are in the range from 87.9(3)° to 88.85(6)° which suggests the pseudo-

octahedral geometry (Figure 8). Complex **7** is a dinuclear and mono-cationic with hexafluorophosphate counter ion. It has two chelating sites with N,N-donor at one site and N,O-donor site at the other. In the first chelating site, Rh(1) is located at 1.766 Å from Cp* and 2.159(4), 2.113(3) and 2.398(13) Å from N(3), O(1) and Cl(1), respectively. In the second chelating site, Rh(2) is located at 1.795 Å from the Cp*, 2.095(4) Å, 2.132(3) Å and 2.397(13) Å from N(1), N(2) and Cl(2), respectively.

The bite angles around the metal at the first chelating centre ranges from 75.79(12)° to 90.44(10)° and at the second chelating centre from 76.07(14)° to 89.24(11)° which support the pseudo-octahedral geometry (Figure 9). It is worth mentioning that the torsion angle at the first chelating center N(1)-C(15)-C(16)-N(2) is 0.90° and that of second chelating center N(3)-N(2)-C(16)-O(1) is 10.99° indicating more strain in the latter. In complex **7**, dichloromethane solvent molecule is found with N-H, O-H, H-Cl interactions with the complex (Figure 10 and Table 3).

Table 3. Selected hydrogen bond distances (Å) and angles (°) of complexes **2**, **3** and **7**.

Complex	D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	< D-H...A (°)
2	C6-H6B...O2 ^a	0.960	2.550	3.509(8)	179
2	O1S-H1S...Cl1 ^b	0.820	2.490	3.285(12)	164
3	C58-H58...O2 ^c	0.960	2.570	3.314(11)	135
7	C24-H24...Cl3 ^d	0.930	2.800	3.631(6)	146

*Symmetry codes: a = 1 - x, 1 - y, 1 - z, b = -x, 2 - y, 2 - z, c = x, -y, 1 - z, d = 1 - x, y, z.

4. Conclusions

A series of Cp* rhodium and Cp* iridium complexes of four Schiff base ligands were synthesized, characterized and their molecular structures were studied by X-ray crystallography. Metal-mediated deprotonation is responsible for the formation of neutral complexes **1–4** where the ligand binds as bidentate in $\kappa^2_{(N,N)}$ binding mode. Complexes **5** and **6** are neutral by virtue of the monodentate nitrogen donor. Complexes **7** and **8** are ionic as the ligand binds through oxygen also as tetradentate $\kappa^4_{(N\cap N\mu N\cap O)}$ donor. Complexes **2**, **3** and **7** were found to have intramolecular π - π interactions and C-H, H-Cl and O-H interactions with solvent molecules and other complexes. We are continuing our search for ligands which can act as mono to multidentate donors containing nitrogen and oxygen donor atoms forming complexes with rhodium and iridium and exhibiting interesting bonding modes and biological activities.

Supplementary Information (SI)

Crystallographic data for the structural analyses of complexes **2**, **3**, **5** and **7** have been deposited with the Cambridge Crystallographic Data Centre bearing the CCDC Nos. 1491082, 1491083, 1519522 and 1491084, respectively. Copies of this information are available on request, free of charge from CCDC, Union Road, Cambridge, CB21EZ, UK (fax: +44-1223- 336-033; e-mail: deposit@ccdc.ac.uk or <http://www.ccdc.cam.ac.uk>). Supplementary Information is available at www.ias.ac.in/chemsci.

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References

- Wang C, Wang J L and Li 2012 W Elucidating Molecular Iridium Water Oxidation Catalysts Using Metal–Organic Frameworks: A Comprehensive Structural, Catalytic, Spectroscopic, and Kinetic Study *J. Am. Chem. Soc.* **134** 19895
- Yang K R, Matula A J, Kwon G, Hong J, Sheehan S W, Thomsen J M, Brudvig G W, Crabtree R H, Tiede D M and Chen L X 2016 Solution Structures of Highly Active Molecular Ir Water-Oxidation Catalysts from Density Functional Theory Combined with High-Energy X-ray Scattering and EXAFS Spectroscopy *J. Am. Chem. Soc.* **138** 5511
- Heiden Z M and Rauchfuss T B 2009 Proton-Assisted Activation of Dihydrogen: Mechanistic Aspects of Proton-Catalyzed Addition of H₂ to Ru and Ir Amido Complexes *J. Am. Chem. Soc.* **131** 3593
- Kawahara R, Fujita K I and Yamaguchi R 2012 Cooperative Catalysis by Iridium Complexes with a Bipyridine Ligand: Versatile Dehydrogenative Oxidation of Alcohols and Reversible Dehydrogenation–Hydrogenation between 2-Propanol and Acetone *Angew. Chem. Int. Ed.* **51** 12790
- Hintermair U, Campos J S, Brewster T P, Pratt L M, Schley N D and Crabtree R H 2013 Hydrogen-Transfer Catalysis with Cp*Ir^{III} Complexes: The Influence of the Ancillary Ligands *ACS Catalysis* **4** 99
- Jiang B, Feng Y and Ison E A 2008 Mechanistic Investigations of the Iridium(III)-Catalyzed Aerobic Oxidation of Primary and Secondary Alcohols *J. Am. Chem. Soc.* **130** 14462
- McSkimming A, Bhadbhade M M and Colbran S B 2013 Bio-Inspired Catalytic Imine Reduction by Rhodium Complexes with Tethered Hantzsch Pyridinium Groups: Evidence for Direct Hydride Transfer from Dihydropyridine to Metal-Activated Substrate *Angew. Chem. Int. Ed.* **52** 3411
- Schäfer S, Ott I, Gust R and Sheldrick W S 2007 Influence of the Polypyridyl (pp) Ligand Size on the DNA Binding Properties, Cytotoxicity and Cellular Uptake of Organoruthenium (II) Complexes of the Type [(η^6 -C₆Me₆), n= 2] *Eur. J. Inorg. Chem.* 3034
- Amouri H, Moussa J, Renfrew A K, Dyson P J, Rager M N and Chamoreau L M 2010 Discovery, Structure, and Anticancer Activity of an Iridium Complex of Diselenobenzoquinone *Angew. Chem. Int. Ed.* **49** 7530
- Starha P, Habtemariam A, Romero-Canelon I, Clarkson G J and Sadler P J 2016 Hydrosulfide Adducts of Organo-Iridium Anticancer Complexes *Inorg. Chem.* **55** 2324
- Gupta G, Das A, Ghate N B, Kim T, Ryu J Y, Lee J, Mandal N and Lee C Y 2016 Novel BODIPY-based Ru(II) and Ir(III) metallarectangles: cellular localization of compounds and their antiproliferative activities *Chem. Commun.* **52** 4274
- Casini A, EDAFE F, Erlandsson M, Gonsalvi L, Ciancetta A, Re N, Ienco A, Messori L, Peruzzini M and Dyson P J 2010 Rationalisation of the inhibition of structurally related organometallic compounds against the drug target cathepsin B by DFT. *Dalton Trans.* **39** 5556
- Gupta G, Prasad K T, Das B, Yap G P and Rao K M 2009 Synthesis, spectral and molecular studies of half-sandwich arene ruthenium and Cp* Rh/Cp* Ir complexes containing bidentate PN and E–N ligands (E= S, Se) based on diphenyl (2-pyridyl) phosphine *J. Organomet. Chem.* **694** 2618
- Rao A V, Prasad K T, Wang P and Rao K M 2012 Study of half-sandwich mono and dinuclear complexes of platinum group metals containing pyrazolyl pyridine analogues: Synthesis and spectral characterization *J. Chem. Sci.* **124** 565
- Mahesh K, Forbes S, Mozharivskyj Y and Rao K M 2015 Half-sandwich η^6 -arene ruthenium and Cp* rhodium/iridium compounds comprising with thioether ligands: Synthesis, spectral and molecular studies. *J. Chem. Sci.* **127** 1135
- Nongbri S L, Das B and Rao K M 2012 Isolation and spectral studies of water-soluble η^5 -cyclichydrocarbon rhodium and iridium complexes with pyridyl diketone

- analogues bonded through $\kappa^2\text{-N} \cap \text{O}$, $\kappa^4\text{-N} \cap \text{O}$, and $\kappa^3\text{-NCN}$ modes *J. Coord. Chem.* **65** 875
17. Almodares Z, Lucas S J, Crossley B D, Basri A M, Pask C M, Hebden A J, Phillips R and McGowan P C 2014 Rhodium, iridium, and ruthenium half-sandwich picolinamide complexes as anticancer agents *Inorg. Chem.* **53** 727
 18. Lucas S J, Lord R M, Basri A M, Allison S J, Phillips R M, Blacker A J and McGowan P C 2016 Increasing anti-cancer activity with longer tether lengths of group 9 Cp^* complexes *Dalton Trans.* **45** 6812
 19. Kar C, Samanta S, Goswami S, Ramesh A and Das G 2015 A single probe to sense Al (III) colorimetrically and Cd (II) by turn-on fluorescence in physiological conditions and live cells, corroborated by X-ray crystallographic and theoretical studies *Dalton Trans.* **44** 4123
 20. Rollas S and Küçükgül S G 2007 Biological activities of hydrazone derivatives *Molecules* **12** 1910
 21. Bernhardt P V, Chin P and Richardson D R 2001 Unprecedented oxidation of a biologically active arylhydrazone chelator catalysed by iron (III): Serendipitous identification of diacylhydrazine ligands with high iron chelation efficacy *J. Biol. Inorg. Chem.* **6** 801
 22. Van Dijken D J, Kovaříček P, Ihrig S P and Hecht S 2015 Unprecedented oxidation of a biologically active aroylhydrazone chelator catalysed by iron (III): Serendipitous identification of diacylhydrazine ligands with high iron chelation efficacy *J. Am. Chem. Soc.* **137** 14982
 23. Geldard J F and Lions F 1963 Tridentate chelate compounds. III *Inorg. Chem.* **2** 270
 24. Pelagatti P, Bacchi A, Carcelli M, Costa M, Frühauf H W, Goubitz K, Pelizzi C, Triclistri M and Vrieze K 2002 Methyl- and Acetyl-palladium (II) Complexes Containing a P, N, O Tridentate Hydrazone Ligand *Eur. J. Inorg. Chem.* **2** 439
 25. Chandrasekhar V, Hossain S, Das S, Biswas S and Sutter J P 2013 Rhombus-shaped tetranuclear [Ln₄] complexes [Ln = Dy (III) and Ho (III)]: Synthesis, structure, and SMM behaviour *Inorg. Chem.* **52** 6346
 26. Pandiarajan D and Ramesh R 2012 Suzuki–Miyaura cross-coupling reaction of aryl bromides catalyzed by palladium (II) pyridoxal hydrazone complexes *J. Organomet. Chem.* **708** 18
 27. Maurya M R, Khurana S, Schulzke C and Rehder D 2001 Dioxo- and Oxovanadium (V) Complexes of Biomimetic Hydrazone ONO Donor Ligands: Synthesis, Characterisation, and Reactivity *Eur. J. Inorg. Chem.* **3** 779
 28. Bernhardt P V, Caldwell L M, Chaston T B, Chin P and Richardson D R 2003 Cytotoxic iron chelators: Characterization of the structure, solution chemistry and redox activity of ligands and iron complexes of the di-2-pyridyl ketone isonicotinoyl hydrazone (HPKIH) analogues *J. Biol. Inorg. Chem.* **8** 866
 29. Singh V, Singh S, Singh D, Singh P, Tiwari K, Mishra M and Butcher R 2013 Synthesis, spectral and single crystal X-ray diffraction studies on Co (II), Ni (II), Cu (II) and Zn (II) complexes with o-amino acetophenone benzoyl hydrazone *Polyhedron* **56** 71
 30. Armarego W L and Chai C L L 2013 Purification of laboratory chemicals Purification of laboratory chemicals, Butterworth-Heinemann.
 31. Chen S L, Liu Z, Xia J H, Li Y H 2012 Development of copper based drugs, radiopharmaceuticals and medical materials *J. Coord. Chem.* **65** 2234
 32. White C, Yates A, Maitlis P and Heinekey D 2007 (η^5 -Pentamethylcyclopentadienyl) Rhodium and Iridium Compounds *Inorg. Synth.* **29** 228
 33. CrysAlis PRO, release 2012 Version 1.171.36.20. Agilent Technologies, Yarnton.
 34. Sheldrick G M 2008 A short history of SHELX *Acta Crystallogr. A* **64** 112
 35. Sheldrick G M 2015 Crystal structure refinement with SHELXL. *Acta Crystallogr. C* **71** 3
 36. Farrugia L J 1997 ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI) *J. Appl. Crystallogr.* **30** 565
 37. Bruno I, Cole J, Edgington P, Kessler M, F, Cabe P M, Pearson J and Taylor R 2002 New software for searching the Cambridge structural database and visualizing crystal structures *Acta. Crystallogr. B* **58** 389
 38. Rao P N, Nongbri S L, Premkumar J R, Verma A K, Bhattacharjee K, Joshi S R, Forbes S H, Mozharivskij Y, Thounaojam R, Aguan K and Rao K M 2015 Synthesis and evaluation of new salicylaldehyde-2-picolinyldhydrazone Schiff base compounds of Ru (II), Rh (III) and Ir (III) as in vitro antitumor, antibacterial and fluorescence imaging agents *J. Biol. Inorg. Chem.* **20** 619
 39. Rao P N, Premkumar J R, Verma A K, Bhattacharjee K, Joshi S R, Forbes S H, Mozharivskij Y and Rao K M 2015 Synthesis, structural, DFT studies and antibacterial evaluation of Cp^* rhodium and Cp^* iridium complexes using hydrazide based dipyriddy ketone ligand *Arabian J. Chem.* **2015**. doi:10.1016/j.arabjc.2015.10.011
 40. Chantzis A, Very T, Despax S, Issenhuth J T, Boeglin A, Hébraud P, Pfeffer M, Monari A and Assfeld X 2014 UV-vis absorption spectrum of a novel Ru (II) complex intercalated in DNA: [Ru (2, 2'-bipy)(dppz)(2, 2'-ArPy)]⁺ *J. Mol. Mod.* **20** 1