Cationic half-sandwich complexes (Rh, Ir, Ru) containing 2-substituted-1,8-naphthyridine chelating ligands: Syntheses, X-ray structure analyses and spectroscopic studies

Herein, we describe the synthesis of twelve $\eta^5$-C$_5$Me$_5$ rhodium, iridium and $\eta^6$-C$_6$H$_6$, $\eta^6$-$\rho$-PrC$_6$H$_4$Me ruthenium complexes incorporating 2-substituted-1,8-naphthyridine ligands; 2-(2-pyridyl)-1,8-naphthyridine (pyNp), 2-(2-thiazolyl)-1,8-naphthyridine (tzNp) and 2-(2-furyl)-1,8-naphthyridine (fuNp).

4.1 Introduction

Mononuclear complexes of platinum group metals containing heterocyclic nitrogen based ligands have received considerable attention owing to their photochemical properties,\textsuperscript{1-9} catalytic activities,\textsuperscript{10-19} electrochemical behaviour,\textsuperscript{20-26} as well as in the development of new biologically active agents.\textsuperscript{27-33} Ruthenium, rhodium and iridium unsubstituted 1,8-naphthyridine based complexes are interesting in their own right of uses as dye – sensitized solar cells and photophysical effects.\textsuperscript{34} The reactivity of these metals with substituted 1,8-naphthyridine based ligands have also been reported. Examples with dinuclear metal-metal bonded compounds,\textsuperscript{35-37} and mononuclear compounds\textsuperscript{38} being known. However no reports dealing with \(\eta^5\)-pentamethylcyclopentadienyl or \(\eta^6\)-arene platinum group metal (Rh, Ir, or Ru) in connectivity with substituted 1,8-naphthyridine ligands have been reported so far.

Herein, we describe the syntheses of twelve \(\eta^5\)-C\textsubscript{5}Me\textsubscript{5} rhodium, iridium and \(\eta^6\)-C\textsubscript{6}H\textsubscript{6}, \(\eta^6\)-p-PrC\textsubscript{6}H\textsubscript{4}Me ruthenium complexes incorporating 2-substituted-1,8-naphthyridine ligands (Chart 4.1); 2-(2-pyridyl)-1,8-naphthyridine (pyNp), 2-(2-thiazolyl)-1,8-naphthyridine (tzNp) and 2-(2-furyl)-1,8-naphthyridine (fuNp). All complexes are characterized by IR, NMR, mass spectrometry and UV/Visible spectroscopy. The molecular structures of five representative complexes are presented as well.
4.2 Experimental

4.2.1 Preparation of ligands (pyNp, fuNp and tzNP).\textsuperscript{39, 40}

4.2.1.1 Preparation of pyNp

500 mg (4.1 mmol) of 2-aminonicotinaldehyde was dissolved in 15 ml of dry ethanol. To this solution was added 0.55 ml (4.95 mmol) of 2-acetylpyridine. The solution was refluxed under nitrogen and treated with three drops of freshly prepared saturated solution of KOH in methanol. After refluxing overnight the solution was concentrated to one third of its original volume and kept in refrigerator to get yellowish crystals. The crystals were isolated by filtration and washed with cold ethanol and dried under vacuum to get pure pyNP.

Yield: 640 mg 75%. \textsuperscript{1}H NMR (CD$_3$CN, $\delta$): 9.09 (dd, 1H), 8.82 (d, 1H), 8.68 (m, 2H), 8.26 (d, 1H), 8.17 (d, 1H), 7.83 (td, 1H), 7.43 (q, 1H), 7.32 (m, 1H).

4.2.1.2 Preparation of tzNp

500 mg (4.1 mmol) of 2-aminonicotinaldehyde was dissolved in 15 ml of dry ethanol. To this solution was added 0.51 ml (4.95 mmol) of 2-acetylthiazole. The solution was refluxed under nitrogen and treated with three drops of freshly prepared saturated solution of KOH in methanol. After refluxing overnight the solution was concentrated to one-third of its original volume and kept in refrigerator to get yellowish crystals. The crystals were isolated by filtration and washed with cold ethanol and dried under vacuum to get pure tzNP.

Yield: 675 mg, 78%. \textsuperscript{1}H NMR (CD$_3$CN, $\delta$): 9.12 (d, 1H), 8.45 (d, 1H), 8.28 (d, 1H), 8.19 (dd, 1H), 7.98 (d, 1H), 7.54 (d, 1H), 7.49 (q, 1H).

4.2.1.3 Preparation of fuNp

The fuNP ligand was synthesized and isolated in a similar manner described for the synthesis of tzNP taking 50 mg (4.1 mmol) of 2-aminonicotinaldehyde and 0.50 ml (5 mmol) of 2-acetyl-furan.

Yield: 660 mg, 82%. \textsuperscript{1}H NMR (CD$_3$CN, $\delta$): 9.07 (dd, 1H), 8.19 (m, 2H), 7.96 (d, 1H), 7.58 (dd, 1H), 7.50 (d, 1H), 7.45 (q, 1H), 6.57 (dd, 1H)
4.2.2 Preparation of complexes 1-6

4.2.2.1 Synthesis of \([\langle \eta^6-C_6H_6 \rangle Ru(pyNp)Cl]\)Cl ([1]Cl)

A mixture of \([\langle \eta^6-C_6H_6 \rangle Ru(\mu-Cl)Cl]\)_2 (50 mg, 0.09 mmol) and pyNp (42 mg, 0.18 mmol) in 10 ml of acetonitrile was refluxed for 90 minutes. A color change from light brown to dark brown was observed. The resulting solution was concentrated under vacuum (2 ml). Then 15 ml of hexane was added to induce precipitation. The yellowish brown solid was filtered off, washed with diethyl ether and dried under vacuum. Yield 80 mg, (87%): C_{19}H_{15}Cl_2N_3Ru (457.31) Calc.: C 49.90, H 3.31, N 9.19; Found: C 50.08, H 3.39, N 9.15. \(^1\)H NMR (CDCl_3, \(\delta\)): 9.56 (d, 1H, \(J_{H-H} = 8\)Hz), 9.38 (q, 1H), 8.76 (d, 1H), 8.58 (m, 2H), 8.48 (d, 1H), 7.91 (td, 1H), 7.90 (q, 1H), 7.78 (td, 1H), 6.15 (s, 6H, C_6H_6). ESI-MS (m/z): 419.8 (100%) [M-Cl]^+.

4.2.2.2 Synthesis of \([\langle \eta^6-C_6H_6 \rangle Ru(tzNp)Cl]\)PF_6 ([2]PF_6)

A mixture of \([\langle \eta^6-C_6H_6 \rangle Ru(\mu-Cl)Cl]\)_2 (50 mg, 0.09 mmol), tzNp (43 mg, 0.20 mmol) and 2.5 equivalents of NH_4PF_6 in 10 ml of acetonitrile was stirred at room temperature for 12 hours. A color change was observed from light brown to yellowish brown during the process. The reaction mixture was filtered off and washed with acetonitrile. The filtrate was reduced under vacuum (2 ml) and 15 ml of diethyl ether was then added to induce precipitation. After standing for 15 minutes, yellow precipitate settled down. The resulting precipitate was filtered, washed with diethyl ether and dried under vacuum. Yield 85 mg (76%): C_{17}H_{13}ClN_3F_6SPRu (572.85) Calc.: C 35.64, H 2.29, N 7.34, S 5.60; Found: C 35.70, H 2.35, N 7.46, S 5.51. \(^1\)H NMR (CD_3CN, \(\delta\)): 9.40 (q, 1H), 8.74 (d, 1H, \(J_{H-H} = 8.12\) Hz, tz-H_1), 8.69 (d, 1H), 8.56 (dd, 1H), 8.24 (d, 1H, \(J_{H-H} = 4\) Hz, tz-H_2), 8.19 (d, 1H), 7.9 (q, 1H), 6.20 (s, 6H, C_6H_6). ESI-MS (m/z): 425.2 (100%) [M-PF_6]^+, 389.4 (20%) [M-PF_6-Cl]^+.

4.2.2.3 Synthesis of \([\langle \eta^6-C_6H_6 \rangle Ru(fuNp)Cl]\)PF_6 ([3]PF_6)

A mixture of \([\langle \eta^6-C_6H_6 \rangle Ru(\mu-Cl)Cl]\)_2 (50 mg, 0.09 mmol), fuNp (36 mg, 0.18 mmol) and 2.5 equivalents of NH_4PF_6 was used and treated following a procedure similar to that described in the synthesis of complex [2]PF_6. The resulting precipitate was filtered, washed with benzene and dried under vacuum.
Yield 70 mg, (63%): C_{12}H_{14}ClF_6N_2OPRu (555.80) Calc.: C 38.90, H 2.54, N 6.38; Found: C 38.70, H 2.45, N 6.46

1H NMR (CDCl_3, δ): 9.52 (dd, 1H), 8.49 (dd, J_H-H = 7.12 Hz, 1H), 8.09 (dd, 1H, J_H-H = 8.08 Hz), 7.84 (d, 1H), 7.71 (d, 1H), 7.67 (q, 1H), 7.57 (q, 1H), 6.81 (q, 1H), 5.93 (S, 6H, C_6H_6); ESI-MS (m/z): 411.1 (100%) [M-PF_6]^+, 374.1 (20%) [M-PF_6-Cl]^+.

4.2.2.4. Synthesis of [(η^6-p-PrC_6H_4Me)Ru(pyNp)Cl]PF_6 ([4]PF_6)

A mixture of [(η^6-p-PrC_6H_4Me)Ru(µ-Cl)Cl]_2 (50 mg, 0.081 mmol), pyNp (34 mg, 0.163 mmol) and 2.5 equivalents of NH_4PF_6 in 10 ml of acetonitrile were stirred at room temperature for 5 h. A white precipitate (NH_4Cl) was removed by filtration. The filtrate was concentrated to 2 ml and diethyl ether was added to induce precipitation. After standing for 15 minutes, an orange-yellowish precipitate was observed. After filtration, the solid was washed with diethyl ether and dried under vacuum.

Yield 82 mg, (81%): C_{23}H_{23}ClF_6N_3PRu (622.93) Calc.: C 44.35, H 3.72, N 6.75; Found: C 44.70, H 3.65, N 6.76

1H NMR (CD_3CN, δ): 9.46 (d, 1H, J_H-H = 12 Hz,), 9.37 (q, 1H, J_H-H = 4 Hz), 8.73 (d, 1H), 8.57 (m, 2H), 8.48 (d, 1H), 8.26 (td, 1H), 7.91 (q, 1H), 7.78 (td, 1H), 6.21 (d, 1H, J_H-H = 5.4 Hz, Ar_p-cy), 6.13 (d, 2H, J_H-H = 6.2 Hz, Ar_p-cy), 5.79 (d,1H, J_H-H = 5.2 Hz, Ar_p-cy), 2.47 (sept, 1H, J_H-H = 4.4 Hz, CH(CH_3)_2), 2.27 (s, 3H, CH_3), 0.91 (d, 3H, CH(CH_3)_2), 0.83 (d, 3H, CH(CH_3)_2); ESI-MS (m/z): 478.3 (100%) [M-PF_6]^+, 440 (8%) [M-PF_6-Cl]^+,

4.2.2.5 Synthesis of [(η^6-p-PrC_6H_4Me)Ru(tzNp)Cl]PF_6 ([5]PF_6)

A mixture of [(η^6-p-PrC_6H_4Me)Ru(µ-Cl)Cl]_2 (50 mg, 0.08 mmol), tzNp (35 mg, 0.17 mmol) and 2.5 equivalents of NH_4PF_6 in 10 ml of methanol was refluxed for 3 h. A color change from brown to yellowish brown was observed. The solution was evaporated and the residue extracted with dichloromethane. The white insoluble material was filtered off. The filtrate was concentrated to 2 ml and diethyl ether was added to induce precipitation. The yellowish orange precipitate was washed with diethyl ether and dried under vacuum.

Yield 80 mg, (78%): C_{21}H_{21}ClF_6 N_3SPRu (628.96) Calc.: C 40.10, H 3.37, N 6.68, S 5.10; Found: C 40.43, H 3.35, N 6.76, S 5.22. 1H NMR (CDCl_3, δ): 9.35 (q, 1H), 8.74 (d, 1H, J_H-H = 3.36 Hz), 8.62 (d, 1H), 8.45 (dd, 1H), 8.15 (d, 1H, J_H-H = 8.32 Hz), 8.06 (d, 1H), 7.86 (q, 1H), 6.31 (d, 1H, J_H-H = 6.2 Hz, Ar_p-cy), 6.26 (d, 1H, J_H-H = 6 Hz, Ar_p-cy),
6.11 (d, 1H, J_{H-H} = 5.68 Hz, Ar_p-cy), 5.99 (d, 1H, J_{H-H} = 6 Hz, Ar_p-cy), 2.79 (sept, 1H, J_{H-H} = 4.14 Hz, CH(CH_{3})_2), 2.28 (s, 3H, CH_{3}), 1.08 (d, 3H, CH(CH_{3})_2), 1.02 (d, 3H, CH(CH_{3})_2); ESI-MS (m/z): 481.9 (100%) [M-PF_{6}]^+, 445.6 (45%) [M-PF_{6}-Cl]^+.

4.2.2.6 Synthesis of [(η^6-p-PrC_{6}H_{4}Me)Ru(fuNp)Cl]PF_{6} ([6]PF_{6})

The reaction of [(η^6-p-PrC_{6}H_{4}Me)Ru(µ-Cl)Cl]_2 (50 mg, 0.08 mmol), fuNp (32 mg, 0.16 mmol) and 2.5 equivalents of NH_{4}PF_{6} was carried out following a procedure similar to that described in the synthesis of [2]PF_{6}.

Yield 70 mg, (70%): C_{22}H_{22}ClF_{6}N_{2}OPRu (611.91) Calc.: C 43.18, H 3.62, N 5.79; Found: C 43.23, H 3.73, N 5.46. \(^1\)H NMR (CD_{3}CN, δ): 9.58 (dd, 1H), 9.05 (dd, 1H), 8.32 (dd, 1H, J_{H-H} = 8.12 Hz), 8.10 (d, 1H), 7.76 (d, 1H), 7.57 (q, H), 6.81 (q, 1H), 5.81 (d, 2H, J_{H-H} = 6.24 Hz, Ar_p-cy), 5.56 (d, 2H, J_{H-H} = 6.14 Hz, Ar_p-cy), 2.86 (sept, 1H, J_{H-H} = 4.04 Hz, CH(CH_{3})_2), 2.16 (s, 3H, CH_{3}), 1.18 (d, 3H, CH(CH_{3})_2), 1.07 (d, 3H, CH(CH_{3})_2); ESI-MS (m/z): 464.9 (100%) [M-PF_{6}]^+, 429.2 (15%) [M-PF_{6}-Cl]^+.

4.2.2.7 Preparation of the cationic complexes 7-12

**General procedure:** A mixture of [(η^5-C_{5}Me_{5})M(µ-Cl)Cl]_2 (0.07 mmol), 2-substituted-1,8-naphthyridine ligand (0.14 mmol) and 2.5 equivalents of NH_{4}PF_{6} in dry methanol (10 ml) was stirred at room temperature for 8 h. The solvent was evaporated under reduced pressure, and the residue was dissolved in dichloromethane. After filtration, the volume was reduced to 2 ml and excess diethyl ether was added to induce precipitation. The precipitate was washed with diethyl ether and dried under vacuum.

4.2.2.7.1 [(η^5-C_{5}Me_{5})Rh(pyNp)Cl]PF_{6} ([7]PF_{6})

Orange-yellow solid, yield 70 mg (79%). C_{23}H_{22}ClF_{6}N_{3}PRh (625.77) Calc.: C 44.14, H 3.87, N 6.71; Found: C 44.70, H 3.75, N 6.76. \(^1\)H NMR (CD_{3}CN, δ): 9.32 (q, 1H, J_{H-H} = 4.08 Hz), 9.03 (d, 1H, J_{H-H} = 4 Hz), 8.78 (d, 1H), 8.55 (m, 2H), 8.5 (d, 1H), 8.29 (td,1H), 7.87 (td, 2H), 1.60 (s, 15H, C_{5}Me_{5}); ESI-MS (m/z): 480.81 (100%) [M-PF_{6}]^+, 444.1 (70%) [M-PF_{6}-Cl]^+.

4.2.2.7.2 [(η^5-C_{5}Me_{5})Rh(tzNp)Cl]PF_{6} ([8]PF_{6})

Orange solid, yield 80 mg (89%). C_{21}H_{22}ClF_{6}N_{3}PRh (628.96) Calc.: C 39.72, H 3.51, N 6.65, S 5.08; Found: C 39.43, H 3.45, N 6.76, S 5.02. \(^1\)H NMR (CD_{3}CN, δ): 9.34 (q, 1H, J_{H-H} = 1.92 Hz), 8.76 (d, 1H, J_{H-H} = 8.4 Hz), 8.57 (dd, 1H), 8.38 (d, 3H), 8.29 (d, 1H, J_{H-H} =
1,8-naphthyridine ligands

$\delta = 8.4 \text{ Hz}$, 8.23 (d, 1H), 7.87 (q, 1H), 1.71 (s, 15H, C$_5$Me$_5$); ESI-MS (m/z): 485.28 (100%) [M-PF$_6$]$^+$, 450.1 (9%) [M-PF$_6^-$ Cl]$^+$. 

4.2.3.3 $[(\eta^5-C_5Me_5)Rh(fuNp)Cl]PF_6$ ([9]PF$_6$)
Orange-yellow solid, yield 68 mg (78%) C$_{22}$H$_{23}$ClF$_6$N$_2$OPRh (614.75) Calc.: C 42.98, H 3.77, N 4.56; Found: C 42.23, H 3.73, N 4.34. $^1$H NMR (CD$_3$CN, $\delta$): 9.42 (dd, 1H), 9.09 (dd, 1H), 8.52 (d, 1H), 8.12 (dd, 1H), 7.79 (d, 1H), 7.76 (d, 1H), 7.67 (q, 1H), 7.52 (q, 1H), 1.55 (s, 15H, C$_5$Me$_5$); ESI-MS (m/z): 468.6 [M-PF$_6$]$^+$, 433.1 (7%) [M-PF$_6^-$ Cl]$^+$. 

4.2.3.4 $[(\eta^5-C_5Me_5)Ir(pyNp)Cl]PF_6$ ([10]PF$_6$)
Orange-yellow solid, yield 80 mg (89%) C$_{23}$H$_{24}$ClF$_6$N$_3$PIr (715.09) Calc.: C 38.63, H 3.38, N 5.58; Found: C 38.70, H 3.55, N 5.66. $^1$H NMR (CDCl$_3$, $\delta$): 9.38 (d, 1H), 9.3 (q, 1H), 8.73 (d, 1H), 8.58 (dd, 1H), 8.37 (d, 3H), 8.31 (d, 1H), 8.21 (d, 1H), 7.89 (q, 1H), 7.87 (td, 1H), 1.71 (s, 15H, C$_5$Me$_5$); ESI-MS (m/z): 569.1 (100%) [M-PF$_6$]$^+$, 533.2 (23%) [M-PF$_6^-$ Cl]$^+$. 

4.2.3.5 $[(\eta^5-C_5Me_5)Ir(tzNp)Cl]PF_6$ ([11]PF$_6$)
Orange-yellow solid, yield 82 mg (91%). C$_{21}$H$_{22}$ClF$_6$N$_3$SPIr (721.11) Calc.: C 34.98, H 3.08, N 5.83, S 4.45; Found: C 34.63, H 3.15, N 5.76, S 4.42. $^1$H NMR (CD$_3$CN, $\delta$): 9.32 (q, 1H), 8.73 (d, 1H), 8.58 (dd, 1H), 8.37 (d, 3H), 8.31 (d, 1H), 8.21 (d, 1H), 7.89 (q, 1H), 1.71 (s, 15H, C$_5$Me$_5$); ESI-MS (m/z): 575.1 (100%) [M-PF$_6$]$^+$, 539.4 (35%) [M-PF$_6^-$ Cl]$^+$. 

4.2.3.6 $[(\eta^5-C_5Me_5)Ir(fuNp)Cl]PF_6$ ([12]PF$_6$)
Orange-yellow solid, yield 61 mg (69%). C$_{22}$H$_{23}$ClF$_6$N$_2$OPIr (704.06) Calc.: C 37.53, H 3.29, N 3.98; Found: C 37.23, H 3.23, N 4.04. $^1$H NMR (CDCl$_3$, $\delta$): 9.40 (dd, 1H), 9.06 (m, 1H), 8.51 (dd, 1H), 8.13 (d, 1H), 7.84 (d, 1H), 7.72 (d, 1H), 7.65 (q, 1H), 7.55 (q, 1H), 1.56 (s, 15H, C$_5$Me$_5$); ESI-MS (m/z): 558.9 (100%) [M-PF$_6$]$^+$, 522.4 (10%) [M-PF$_6^-$ Cl]$^+$. 

4.2.4 Single crystal X-ray structure analyses

In [10]PF$_6$ a positive residual electron density of 11.43 eÅ$^{-3}$ (0.80 Å from Iridium) and electron density hole of -4.61 eÅ$^{-3}$ (0.66 Å from Iridium) surrounded the heavy iridium atom. Crystallographic details are summarised in Table 4.1.
4.3 Results and Discussion

4.3.1 Syntheses

The dinuclear arene ruthenium complexes \([(\eta^6\text{-arene})\text{Ru(\mu-Cl)Cl}]_2\) (arene = C\(_6\)H\(_6\), \(p^1\text{-PrC}_6\text{H}_4\text{Me}\)) react in acetonitrile with the 2-substituted-1,8-naphthyridine ligands - 2-(2-pyridyl)-1,8-naphthyridine (pyNp), 2-(2-thiazolyl)-1,8-naphthyridine (tzNp) and 2-(2-furyl)-1,8-naphthyridine (fuNp) to give the mononuclear cationic complexes \([(\eta^6\text{-C}_6\text{H}_6)\text{Ru(L)Cl}]^+\) \{L = pyNp (1); tzNp (2); fuNp (3)}\}, \([(\eta^6\text{-p-PrC}_6\text{H}_4\text{Me})\text{Ru(L)Cl}]^+\) \{L = pyNp (4); tzNp (5); fuNp (6)}\} (Scheme 4.1). Cation 1 is isolated as its chloro salt, while the other cationic ruthenium complexes are obtained as their hexafluorophosphate salts.

![Scheme 4.1](image-url)

Similarly, the reaction in methanol of the dimeric chloro-bridged complexes \([(\eta^5\text{-C}_5\text{Me}_5)\text{M(\mu-Cl)Cl}]_2\) (M = Rh, Ir) with the same 2-substituted-1,8-naphthyridine ligands leads to the formation of the mononuclear cationic complexes \([(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(L)Cl}]^+\) \{L = pyNp (7); tzNp (8); fuNp (9)}\} and \([(\eta^5\text{-C}_5\text{Me}_5)\text{Ir(L)Cl}]^+\) \{L = pyNp (10); tzNp (11); fuNp (12)}\} (Scheme 4.2). All rhodium and iridium complexes are isolated as their hexafluorophosphate salts.
All complexes are orange yellow in color, non-hygroscopic, air stable solids. However, the complexes with the fuNp ligand (3, 6, 9 and 12) are unstable in solution. They are soluble in acetonitrile but partially soluble in dichloromethane, chloroform and acetone. The reactions of pyNp and tzNp with the dinuclear rhodium and iridium precursors are instantaneous as compared to those with the ruthenium precursors. However, the reaction is comparatively slow for fuNp with these dinuclear precursors.

The infrared spectra of the complexes 2-12 exhibit a strong band in the region 844-850 cm\(^{-1}\), a typical \(\nu_{P-F}\) stretching band for the PF\(_6\) anions. Moreover, all complexes show absorption bands at 1600-1610 cm\(^{-1}\) and 1470-1474 cm\(^{-1}\) for the \(\nu_{C=C}\) and \(\nu_{C=N}\) vibrations of the 1,8-naphthyridine moiety.\(^{41}\) The complexes 2, 5, 8 and 11 show two additional absorption bands at 1450-1452 cm\(^{-1}\) and 1480-1484 cm\(^{-1}\) corresponding to the \(\nu_{C=N}\) and \(\nu_{C=S}\) stretching frequency of the thiazolyl group. The complexes 3, 6, 9 and 12 show a characteristic absorption band at 1626-1630 cm\(^{-1}\) which correspond to \(\nu_{C=C}\) of the furyl group. The mass spectra of all these complexes exhibited corresponding molecular
ion peaks. For instance the mass spectra of complexes 3 and 4 have been depicted in figure 4.1 and 4.2 respectively.

Figure 4.1: Mass spectrum of complex \([(\eta^6-C_6H_6)Ru(fuNp)Cl]PF_6 ([3]PF_6)\]

Figure 4.2: Mass spectrum of complex \([(\eta^6-p^1PrC_5H_4Me)Ru(pyNp)Cl]PF_6 ([4]PF_6)\]
4.3.2 NMR spectrometry

The $^1$H NMR spectra of the benzene, $p$-cymene and pentamethylcyclopentadienyl derivatives which have pyNp, tzNp and fuNp as ligands exhibit nine resonances in the region $\delta = 9.56$ to 7.78, seven resonances around $\delta = 9.41$ to 7.90, and eight resonances around $\delta = 9.58$ to 6.68 in the aromatic region, respectively. In addition to these signals, complexes 1, 2 and 3 exhibit a singlet resonance for the benzene ring protons at $\delta = 6.20$ to 5.93. Complexes 4, 5 and 6 exhibit an unusual pattern of resonances for the $p$-cymene ligand. For instance, the methyl protons of the isopropyl group displays two doublets at ca. $\delta = 1.18$ to 1.07, instead of one doublet (see Figure 4.3 and 4.4) as in the starting complex. The aromatic protons of the $p$-cymene ligand displays three doublets for complex 4 (see Figure 4.3) and four doublets for complex 5 (see Figure 4.4) at ca. $\delta = 6.31$ to 5.79, instead of two doublets as in the starting precursor. This unusual pattern is due to the diastereotopic methyl protons of the isopropyl group and aromatic protons of the $p$-cymene ligand, since the ruthenium atom is stereogenic due to the coordination of four different ligand atoms. The other reason could be due to the loss of planarity of the $p$-cymene ligand, because of the steric nature of the ligand.

Figure 4.3: $^1$H NMR spectrum of complex 4 in acetonitrile-$d_3$. 
1,8-naphthyridine ligands

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Figure 4.4: $^1$H NMR spectrum of complex 5 in acetonitrile-$d_3$.

All these complexes show downfield shift for all protons compared to the starting precursors, which might result from the charge transfer from metal centre to naphthyridine-based ligands such as pyNp and tzNp. Complexes 7 to 12 exhibit a singlet resonance at $\delta = 1.71$ to 1.55 for the five methyl groups of the pentamethylcyclopentadienyl ligand.

4.3.3 X-ray structural study

The molecular structure of the benzene derivatives [(η⁶-C₆H₆)Ru(pyNp)Cl]Cl or [1]Cl and [(η⁶-C₆H₆)Ru(tzNp)Cl]PF₆ or [2]PF₆, the $p$-cymene derivatives [(η⁶-$p$-iPrC₆H₄Me)Ru(pyNp)Cl]PF₆ or [4]PF₆ and [(η⁶-$p$-iPrC₆H₄Me)Ru(tzNp)Cl]PF₆ or [5]PF₆ as well as the pentamethylcyclopentadienyl iridium complex [(η⁵-C₅Me₅)Ir(pyNp)Cl]PF₆ or [10]PF₆ have been established by single crystal X-ray structure analysis. All cationic complexes show a typical piano-stool geometry with the metal centre being coordinated by an aromatic ligand, a terminal chloro ligand and a chelating 2-substituted-1,8-naphthyridine ligand. Formally, the 2-substituted-1,8-naphthyridine ligand can coordinate to the metal centre either through one or two nitrogen atoms of the naphthyridine moiety or through the N, O or S atoms of the 2-substituted ring. Interestingly, in this study, all metal centres were found to be coordinated to the 2-substituted-1,8-naphthyridine ligand in a five-membered ring chelating fashion involving one nitrogen atom of the naphthyridine moiety and the nitrogen atom of the 2-pyridyl or 2-thiazolyl group and the
1,8-naphthyridine ligands

oxygen atom of the 2-furyl group. Indeed, in [1]Cl, [4]PF₆ and [10]PF₆ the pyNp ligand is found as a five-membered ring N,N-chelating ligand (see Figure 4.5 to 4.6).

![Figure 4.5: ORTEP diagram of cations 1 and 4 at 35% probability level, chloride anion and hydrogen atoms being omitted for clarity.](image)

Similarly, in [2]PF₆ and [5]PF₆, the tzNp ligand is found to coordinate through the N1 atom of the naphthyridine moiety and the N3 atom of the 2-substituted thiazolyl ring to generate a five-membered ring metallo-cycle (see Figure 4.7). In these tzNp
complexes, the S atom points away from the metal centre and show no interaction with neighbouring cations. Selected bond lengths and angles for $[1]\text{Cl} \cdot 3\text{H}_2\text{O}$, $[2]\text{PF}_6$, $[4]\text{PF}_6$, $[5]\text{PF}_6$ and $[10]\text{PF}_6$ are presented in Table 4.2.

Figure 4.7: ORTEP diagram of cations 2 and 5 at 50% probability level, hexafluorophosphate anion and hydrogen atoms being omitted for clarity.

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<td>C₁₉H₂₃Cl₂N₃O₅Ru</td>
<td>C₁₇H₁₂ClF₆N₃PRuS</td>
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<td>P 2/c (no. 14)</td>
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<td>Crystal color, shape</td>
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<td>orange rod</td>
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<td>a (Å)</td>
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<td>b (Å)</td>
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<td>β (°)</td>
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<td>γ (°)</td>
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<td>V (Å³)</td>
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<td>0.0242, wR₂ 0.0612</td>
<td>0.0551, wR₂ 0.1013</td>
<td>0.0320, wR₂ 0.0821</td>
<td>0.0737, wR₂ 0.1907</td>
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<td>0.0304, wR₂ 0.0648</td>
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<td>0.529, -0.929</td>
<td>0.639, -0.897</td>
<td>1.443, -0.6341</td>
<td>1.432, -4.606</td>
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* Structures were refined on F₀²: wR₂ = [Σ [w(F₀² - F_c²)²] / Σw(F₀²)²]¹/², where w⁻¹ = [Σ (F₀²)² + (aP)² + bP] and P = [max(F₀², 0) + 2F_c²]/3

<table>
<thead>
<tr>
<th></th>
<th>1 (pyNp)</th>
<th>2 (tzNp)</th>
<th>4 (pyNp)</th>
<th>5 (tzNp)</th>
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<td><strong>Distances (Å)</strong></td>
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<td>M-Cl</td>
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<td>M-N1</td>
<td>2.109(3)</td>
<td>2.123(2)</td>
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<td>M-N3</td>
<td>2.088(2)</td>
<td>2.091(2)</td>
<td>2.078(6)</td>
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<td>M-centroid(^a)</td>
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<td>1.67</td>
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<td>C8-C9</td>
<td>1.478(4)</td>
<td>1.448(4)</td>
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<td><strong>Angles (º)</strong></td>
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<td>N3-M-Cl</td>
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<td>86.12(6)</td>
<td>84.9(2)</td>
<td>86.24(7)</td>
<td>87.4(3)</td>
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</tbody>
</table>

\(^a\) Calculated centroid of the C\(_5\) or C\(_6\) coordinated aromatic ring.

The distances between the ruthenium atom and the centroid of the C\(_6\) aromatic ring in 1, 2, 4 and 5 are comparable (1.67 to 1.69 Å) but quite shorter than the distance between the iridium atom and the C\(_5\) aromatic ring observed in 10 (1.79 Å). The M-N1 bond distances [2.107(9) to 2.152(2) Å] are comparable to those in [(η⁶-p-iPrC\(_6\)H\(_2\)Me)RuCl(2,3-bis(2-pyridyl)pyrazine)]BF\(_4\),\(^44\) [(η⁵-C\(_5\)H\(_6\))IrCl(2-(1-imidazol-2-yl)pyridine)]PF\(_6\),\(^45\) and [(η⁵-C\(_5\)Me\(_5\))Ir(2-(2'-pyridyl)imidazole)Cl]PF\(_6\),\(^46\). The Ir-N3 bond distance (2.136(9) Å) in 10 is slightly longer than the corresponding distances in the ruthenium complexes 1, 2, 4 and 5 (2.073(2) to 2.091(2) Å), while the M-Cl bond lengths show no significant differences among the five cations. However, a noticeable difference is observed in the distances of the C8-C9 connecting bond (naphthyridine 2-substituted ring C-C bond). In the tzNp derivatives, the C8-C9 distances [1.448(4) in 2 and 1.444(4) Å in 5] are shorter than those found in the pyNp derivatives 1, 4 and 10 [1.478(4), 1.485(9) and 1.51(2) Å] respectively.

Complex [1]Cl crystallises with three molecules of water per asymmetric unit, forming an intricate hydrogen-bonded network around the chloride atom. It involves the three water molecules and some hydrogen atoms of the pyNp and C\(_6\)H\(_6\) ligands (see
Figure 4.8). The O-O and O-C distances of the hydrogen bonds range from 3.12 to 3.77 Å, with O-H···O or C-H···O angles ranging from 137.6 to 177.0°.

Figure 4.8: Hydrogen-bonded network observed in [1]Cl · 3 H₂O with H-Cl distances.

In the crystal packing of [10]PF₆, two cationic molecules of 10 form a dimer through π-stacking interactions (see Figure 4.9). The distance observed between the two π-stacking interacting systems (centroid···centroid 3.62 Å) is in good agreement with the theoretical value calculated for a slipped parallel stacking mode.⁴⁷
4.3.4 UV/Visible spectroscopy

Electronic absorption spectral data of selected complexes at 10^{-5} M concentration in the range 320-520 nm are summarised in Table 4.3. The spectra of these complexes are characterized by two main features, \textit{viz.}, an intense ligand-localized or intra-ligand \( \pi \rightarrow \pi^* \) transition in the ultraviolet region and metal-to-ligand charge transfer (MLCT) \( d\pi(M) \rightarrow \pi^* \) (Np-based ligands) bands in the visible region\(^{48}\). Since the low spin \( d^6 \) configuration of the mononuclear complexes provides filled orbitals of proper symmetry at the Ru(II), Rh(III) and Ir(III) centres, these can interact with low lying \( \pi^* \) orbitals of the ligands. All these complexes show two absorption bands in the region 340-390 nm, while the complexes bearing fuNp ligand (N,O donor) exhibit two absorption bands in blue shift at 330-355 nm, the second being a shoulder of the first band. It shows a series of ligand-centred \( \pi - \pi^* \) transitions with high intensity absorption bands in the UV region. One should therefore expect a band attributable to the metal-to-ligand charge transfer (MLCT) \( (t_{2g} - \pi^*) \) transitions in their electronic spectra\(^{49-52}\). All these complexes exhibit a broad absorption band with low intensity and low energy at 420-440 nm, while the complexes bearing fuNp ligand exhibit a very low intensity shoulder in the near visible region.

Figure 4.9: Dimeric structure of [10]PF\(_{6}\) showing the separation of the \( \pi \)-stacking system.
region 385 – 390 nm, which originate from dπ (Ru, Rh and Ir) → π* (naphthyridine based ligands) metal-to-ligand charge transfer transitions. Representative spectra of these complexes are presented in Figure 4.10.

![Figure 4.10: Selected UV/Visible electronic spectrum in acetonitrile at 298 K.](image)

Table 4.3: UV/Visible data for selected complexes in acetonitrile at 298 K.

<table>
<thead>
<tr>
<th>No.</th>
<th>Complex</th>
<th>λ_{max} (nm) / ε 10^{-3} M^{-1} cm^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>[(η^6-C_{6}H_{6})Ru(tzNp)Cl]^+</td>
<td>342 (0.30) 357 (0.37) 422 (0.12)</td>
</tr>
<tr>
<td>3</td>
<td>[(η^6-C_{6}H_{6})Ru(fuNp)Cl]^+</td>
<td>338 (0.70) 352 (sh) 385 (sh) (10^{-3} M^{-1} cm^{-1})</td>
</tr>
<tr>
<td>5</td>
<td>[(η^6-p-PrC_{6}H_{4}Me)Ru(tzNp)Cl]^+</td>
<td>342 (0.34) 357 (0.37) 435 (0.11)</td>
</tr>
<tr>
<td>7</td>
<td>[(η^{5}-C_{3}Me_{3})Rh(pyNp)Cl]^+</td>
<td>342 (0.24) 385 (0.25) 436 (0.11)</td>
</tr>
<tr>
<td>9</td>
<td>[(η^{5}-C_{3}Me_{3})Rh(fuNp)Cl]^+</td>
<td>334 (0.41) 348 (sh) 390 (sh)</td>
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</table>

4.4 Conclusion

In this work we demonstrated that all metal centres are coordinated to the 2-substituted-1,8-naphthyridine ligand in a five-membered ring chelating fashion involving one nitrogen atom of the naphthyridine moiety and the nitrogen atom of the 2-pyridyl or 2-thiazolyl group and the oxygen atom of the 2-furyl group. The formation of
bridging complexes with the remaining nitrogen atom of the naphthyridine moiety was unsuccessful in our hand.

4.5 Supplementary material


References

1,8-naphthyridine ligands


