CHAPTER 5

Reactivity Studies of Cyclopentadienyl
Ruthenium(II), Osmium(II) and Pentamethyl-cyclopentadienyl Iridium(III) Complexes Towards 2-
(2’-Pyridyl)Imidazole Derivatives

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Reactivity studies of cyclopentadienyl ruthenium (II), osmium (II) and pentamethylocyclopentadienyl iridium(III) complexes towards 2-(2'-pyridyl)imidazole derivatives.

Abstract

The reaction of \([\eta^5-C_5H_5]Ru(PPh_3)_2Cl\] and \([\eta^5-C_5H_5]Os(PPh_3)_2Br\] with chelating 2-(2'-pyridyl)imidazole \(N\cap N\) ligands and \(NH_4PF_6\) yields cationic complexes of the type \([\eta^5-C_5H_5]M(N\cap N)(PPh_3)]^+\) (1: \(M = Ru, N\cap N = 2-(2'-pyridyl)imidazole; 2: M = Ru, N\cap N = 2-(2'-pyridyl)benzimidazole; 3: M = Ru, N\cap N = 2-(2'-pyridyl)-4,5-dimethylimidazole; 4: M = Ru, N\cap N = 2-(2'-pyridyl)-4,5-diphenylimidazole; 5: M = Os, N\cap N = 2-(2'-pyridyl)imidazole; 6: M = Os, N\cap N = 2-(2'-pyridyl)benzimidazole). They have been isolated and characterized as their hexafluorophosphate salts. Similarly, in the presence of \(NH_4PF_6\), \([\eta^5-C_5Me_5]Ir(\mu-Cl)Cl\] reacts in dry methanol with \(N\cap N\) chelating ligands to afford in excellent yield \([\eta^5-C_5Me_5]Ir(N\cap N)Cl]PF_6\) (7: \(N\cap N = 2-(2'-pyridyl)imidazole; 8: N\cap N = 2-(2'-pyridyl)benzimidazole). All the compounds have been characterized by infrared and NMR spectroscopy and the molecular structure of \([1]PF_6, [2]PF_6\) and \([7]PF_6\) by single-crystal X-ray structure analysis.

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5.1 Introduction

The chemistry of cyclopentadienyl bisphosphine ruthenium complexes [(η⁵-C₅H₅)Ru(PPh₃)₂X] is the family of an area of active research [1] due to their high reactivity and catalytic activities [2-3]. These properties have prompted widespread interest regarding both the synthetic applications and the mechanistic features of cyclopentadienyl complexes for a large number of transition metals. Similarly, there is an increasing interest in the organometallic chemistry of osmium as the nature of the differences from its lighter congener ruthenium becomes more apparent [4]. However, the complex [(η⁵-C₅H₅)Os(PPh₃)₂Br] chemistry have not been studied extensively due to lower kinetic labiality of the triphenylphosphines compared to its ruthenium analogue [5]. Until recently far fewer studies had been carried out on pentamethylcyclopentadienyl rhodium(III) and iridium(III) complexes with chelating N₉N-donor bases [6]. The chemistry of [(η⁵-C₅H₅)Ru(PPh₃)₂Cl] is characterized by facile displacement of either chloride or one or both triphenylphosphine ligands, affording cationic or neutral compounds, respectively, depending on the solvent and reaction conditions [7]. The electron rich metal center contributes to the stabilization of unusual ligands such as vinylidines and allenylidines [8]. We had reported that the reactions of cyclopentadienyl ruthenium (II), [(η⁵-C₅Mes)Ru(PPh₃)₂(CH₃CN)]⁺ and [(η⁵-C₅H₅)Ru(PPh₃)₂(CH₃CN)]⁺ [9] with a variety of nitrogen based ligands. In this paper, as a part of our continuing study, we would like to report the syntheses and characterization of new cationic cyclopentadienyl (Cp) ruthenium(II), osmium(II) and pentamethylcyclopentadienyl (Cp*) iridium(III) complexes with chelating N₉N-donor ligands [L₁ = 2-(2'-pyridyl)imidazole, L₂ = 2-(2'-pyridyl)benzimidazole, L₃ = 2-(2'...
pyridyl)-4,5-dimethylimidazole, $L_4 = 2$-(2'-pyridyl)-4,5-diphenylimidazole) (Scheme 5.1). In order to confirm the nature of bonding, the molecular structures of $[(\eta^5-C_5H_5)Ru\{2-(2'\text{-pyridyl})imidazole\}(PPh_3)]PF_6$ ([1]PF$_6$), $[(\eta^5-C_5H_5)Ru\{2-(2'\text{-pyridyl})benzimidazole\}(PPh_3)]PF_6$ ([2]PF$_6$), and $[(\eta^5-C_5Me_5)Ir\{2-(2'\text{-pyridyl})imidazole\}]Cl\[PF_6$ ([7]PF$_6$) have been solved by x-ray crystallography.

![Scheme 5.1: Ligands and numbering scheme used in this study.](image)

5.2. Experimental

Elemental analyses were performed on a Perkin-Elmer-2400 CHN/O analyzer. Infrared spectra were recorded on a Perkin-Elmer Model 983 spectrophotometer with the sample prepared as KBr pellets. The $^1$H NMR spectra were recorded on a Bruker ACF-300 (300 MHz) spectrometer in CDCl$_3$ solvents with TMS as internal reference. All chemicals used were of reagent grade. All reactions were carried out in distilled and dried solvents. Ruthenium trichloride, iridium trichloride and osmium tetraoxide were purchased from Arora Matthey Ltd and Aldrich. The 2-(2'-pyridyl)imidazole and its derivatives were prepared by following a literature procedure [10]. 2-(2'-Pyridyl)benzimidazole (Aldrich), pyridine-2-aldehyde (Fluka), glyoxal (Aldrich), 2,3-butanedione (Aldrich) and benzyl (Sd Fine) were used as received. The precursor's complexes $[(\eta^5-$
C₅H₅)Ru[(PPh₃)₂Cl]. [(η⁵-C₅H₅)Os(PPh₃)₂Br] [11] and [(η⁵-C₅Me₅)Ir(μ-Cl)Cl]₂ [12]
were prepared by following the reported literature methods.

5.2.1. Synthesis of [(η⁵-C₅H₅)Ru(NNN)(PPh₃)]PF₆

The following general procedure was used for the preparation of complexes [1]PF₆ to [4]PF₆.

Preparation of [1]PF₆: A mixture of [(η⁵-C₅H₅)Ru(PPh₃)₂Cl] (0.1 g, 0.14 mmol), 2-(2'-
pyridyl)imidazole (0.04, 0.28 mmol) and NH₄PF₆ (0.046 g, 0.28 mmol) was refluxed in
dry methanol (20 ml) under a nitrogen atmosphere for 6 hrs. The yellow suspension
turns to a light yellow color. The solvent is evaporated at reduced pressure. Then the
residue was dissolved in dichloromethane (5 ml), and the solution filtered to remove
ammonium chloride. The yellow solution was concentrated (2 ml) and by addition of an
excess of hexane the orange yellow product precipitates. The compound is filtered and
dried under vacuum to give [1]PF₆.

Complex [(η⁵-C₅H₅)Ru{2-(2'-pyridyl)imidazole}(PPh₃)]PF₆ [1]PF₆

Yield: 63 mg, 64 %.

Elemental Anal (%) Calc. for C₃₁H₂₇N₃F₆P₂Ru: C, 51.81; H, 3.76; N, 5.85.

Found: C, 51.54; H, 4.17; N, 5.44.

IR (KBr pellets, cm⁻¹): 1606 (νC=C), 1480, 1440 (νC=N), 857 (νPF₆).

¹H NMR (CDCl₃, δ): 12.01 (s, 1H, NH); 9.04 (d, J_H-H = 5.74 Hz, 1H, H₆); 8. 75 (d, J_H-H =
6.08 Hz, H₇); 8.50 (d, J_H-H = 6.02 Hz, H₅); 8.00 (d, J_H-H = 5.12 Hz, 1H, H₃); 7.78 (m.
15H, Ph); 7.70 (t, 1H, H₄); 7.32 (t, 1H, H₃); 4.68 (s, 5H, C₅H₅).
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**Complex \[\eta^5-C_3H_5\]Ru[2-(2'-pyridyl)benzimidazole]PF_6 [2]PF_6**

Yield: 65 mg, 62%.

Elemental Anal (%) Calc. for C_{35}H_{29}F_6P_2N_3Ru: C, 54.69; H, 3.78; N, 5.47; found: C, 54.87; H, 4.12; N, 5.67.

IR (KBr pellets, cm\(^{-1}\)): 1613 (\(\nu_{C=C}\)), 1447 (\(\nu_{C=N}\)), 850 (\(\nu_{P\-F}\)).

\(^1\)H NMR (CDCl\(_3\), \(\delta\)): 8.74 (d, \(J_{HH} = 5.42\)Hz, 1H, H\(_6\)); 8.07 (d, \(J_{HH} = 5.80\)Hz, 1H, H\(_3\)); 7.98 (t, 1H, H\(_4\)); 7.90 (t, 1H, H\(_5\)); 7.48 (m, 15H, Ph); 7.32 (m, 4H, H\(_7-10\)); 4.64 (s, 5H, C\(_5\)H\(_5\)).

**Complex \[\eta^5-C_3H_5\]Ru[2-(2'-pyridyl)-4,5-dimethylimidazole]PF_6 [3]PF_6**

Yield: 64 mg, 62%.

Elemental Anal. (%) Calc for C\(_{33}\)H\(_{31}\)F\(_6\)P\(_2\)N\(_3\)Ru: C, 53.08; H, 4.16; N, 5.63; found: C, 53.28; H, 4.66; N, 5.77.

IR (KBr pellets, cm\(^{-1}\)): 1604 (\(\nu_{C=C}\)), 1480, 1447 (\(\nu_{C=N}\)), 855 (\(\nu_{P\-F}\)).

\(^1\)H NMR (CDCl\(_3\), \(\delta\)): 8.50 (d, \(J_{HH} = 5.74\)Hz, 1H, H\(_6\)); 8.18 (d, \(J_{HH} = 5.00\)Hz, 1H, H\(_3\)); 7.53 (m, 15H, Ph); 7.39 (t, 1H, H\(_4\)); 7.28 (t, 1H, H\(_5\)); 4.67 (s, 5H, C\(_5\)H\(_5\)); 3.21 (s, 6H, CH\(_3\)).

**Complex \[\eta^5-C_3H_5\]Ru[2-(2'-pyridyl)-4,5-diphenylimidazole]PF_6 [4]PF_6**

Yield: 70 mg, 60%.

Elemental Anal (%), Calc for C\(_{43}\)H\(_{35}\)N\(_3\)F\(_6\)Ru: C, 59.31; H, 4.02, N, 4.83; found: C, 60.23; H, 4.23; N, 5.13.

IR (KBr pellets, cm\(^{-1}\)): 1600 (\(\nu_{C=C}\)), 1480, 1440 (\(\nu_{C=N}\)), 850 (\(\nu_{P\-F}\)).

\(^1\)H NMR (CDCl\(_3\), \(\delta\)): 8.50 (d, \(J_{HH} = 5.0\)Hz, 1H, H\(_6\)); 8.27 (d, \(J_{HH} = 5.73\)Hz, 1H, H\(_3\)). 7.92 (m, 25H, Ph); 7.60 (t, 1H, H\(_4\)); 7.37 (t, 1H, H\(_5\)); 4.62 (s, 5H, C\(_5\)H\(_5\)).
5.2.2. Synthesis of $[(\eta^5-C_5H_5)M(N\cap N)(PPh_3)]PF_6$

These complexes were prepared by the same method given in section 2.1 using of $[(\eta^5-C_5H_5)Os(PPh_3)_2(CH_3CN)]PF_6$ instead of $[(\eta^5-C_5H_5)Ru(PPh_3)_2Cl]$.

**Complex $[(\eta^5-C_5H_5)Os\{2-(2'-pyridyl)imidazole\}(PPh_3)]PF_6$ [5]PF_6**

Yield: 48 mg, 57%.

Elemental analysis (%) for C$_{31}$H$_{27}$N$_3$P$_2$F$_6$O$_s$. Calc.: C, 46.09; H, 3.35; N, 5.21; found: C, 46.36; H, 4.03; N, 5.65.

IR (KBr pellets, cm$^{-1}$): 1600 (vC=C), 1480, 1440 (vC=N), 885 (vP-F)

$^1$H NMR (CDCl$_3$, $\delta$): 8.95 (d, $J_{H-H} = 5.7$ Hz, 1H, H$_6$); 8.78 (d, $J_{H-H} = 6.05$ Hz, 1H, H$_3$); 8.63 (d, $J_{H-H} = 6.12$ Hz, 1H, H$_7$); 8.59 (d, $J_{H-H} = 5.52$ Hz, 1H, H$_8$); 7.89 (m, 15H, Ph); 7.75 (t, 1H, H$_4$); 7.48 (t, 1H, H$_5$); 4.59 (s, 5H, C$_5$H$_5$).

**Complex $[(\eta^5-C_5H_5)Os\{2-(2'-pyridyl)benzimidazole\}(PPh_3)]PF_6$ [6]PF_6**

Yield: 46 mg, 52%.

Elemental analysis (%) for C$_{35}$H$_{29}$N$_3$P$_2$F$_6$O$_s$. Calc.: C, 49.01; H, 3.38; N, 4.90; found: C, 49.15; H, 3.56; N, 5.15.

IR (KBr pellets, cm$^{-1}$): 1613 (vC=C), 1447 (vC=N), 850 (vP-F).

$^1$H NMR (CDCl$_3$, $\delta$): 8.50 (d, $J_{H-H} = 5.2$ Hz, 1H, H$_6$); 8.10 (d, $J_{H-H} = 5.2$ Hz, 1H, H$_3$); 7.0-7.27 (m, 15H, Ph); 7.9 (t, 1H, H$_4$); 7.45 (t, 1H, H$_5$); 7.37 (q, 4H, H$_{7,10}$); 4.65 (s, 5H, C$_5$H$_5$).

5.2.3. Synthesis of $[(\eta^5-C_5Me_5)Ir(N\cap N)Cl]PF_6$

These complexes were prepared by the same method given in section 2.1 using 0.5 equivalent of $[(\eta^5-C_5Me_5)Ir(\mu-Cl)Cl]_2$ instead of 1 equivalent of $[(\eta^5-C_5H_5)M(PPh_3)_2Cl]$.
Complex [(η^5-C_5Me_5)Ir{2-(2'-pyridyl)imidazole}Cl]PF_6 [7]PF_6

Yield: 52 mg, 64%.

Elemental Anal (%), Calc for: C_{18}H_{22}ClN_3F_6Pir. Calc.: C, 33.13; H, 3.37; N, 6.44; found: C, 32.87; H, 3.88; N, 6.23.

IR (KBr pellets, cm\(^{-1}\)): 1600 (ν_C=C), 1460-1327 (ν_C=N), 850 (ν_P-F).

\(^1\)H NMR (CDCl_3, δ): 8.94 (d, J_H-H = 6.4 Hz, 1H, H_6); 8.50 (d, J_H-H = 6.12 Hz, 1H, H_3); 8.00 (d, J_H-H = 6.03 Hz, 1H, H_7); 7.90 (d, J_H-H = 5.23 Hz, 1H, H_8); 7.73 (t, 1H, H_4); 7.43 (t, 1H, H_5); 1.9 (s, 15H, C_5Me_5)

Complex [(η^5-C_5Me_5)Ir{2-(2'-pyridyl)benzimidazole}Cl]PF_6 [8]PF_6

Yield: 54 mg, 62%.

Elemental Anal (%), Calc for: C_{22}H_{24}ClN_3F_6Pir. Calc.: C, 37.61; H, 3.42; N, 5.98; found: C, 37.52; H, 3.87; N, 6.15.

IR (KBr pellets, cm\(^{-1}\)): 1600 (ν_C=C), 1474-1407 (ν_C=N), 850 (ν_P-F).

\(^1\)H NMR (CDCl_3, δ): 8.97 (d, J_H-H = 5.63 Hz, 1H, H_6); 8.90 (d, J_H-H = 5.29 Hz, 1H, H_3); 7.85 (t, 1H, H_4); 7.43 (t, 1H, H_5); 7.24 (m, 4H, H_1-4); 1.82 (s, 15H, C_5Me_5)

5.2.3. Single-crystal X-ray structures analyses

reciprocal sphere equipped with a CCD detector, X-ray intensity data were collected with Mo-Kα graphite monochromated radiation at 120 (2) K, with 0.3°ω scan mode and 10 second per frame. The intensity data were corrected for Lorenz and polarization effects. The structures were solved by direct methods using the program SHELXS-97 [13]. Refinement and all further calculations were carried out using SHELXL-97 [14].

The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-square on \( F^2 \). In [2]PF₆ H₂O, the \(-C₅H₄NC₃N₂H-\) fragment of the 2-(2'-pyridyl)benzimidazole was found to be disordered over two positions and the partial occupancy factor was refined at 76:24. Crystallographic details are summarized in Table 1. Figures 1, 2 and 4 are drawn with ORTEP32 [15] while Figures 3 and 5 are drawn with MERCURY [16].

5.3. Results and discussion

The reactions in dry methanol of [(η⁵-C₅H₅)Ru(PPh₃)₂Cl] and [(η⁵-C₅H₅)Os(PPh₃)₂Br] with an excess of chelating NnN ligands and NH₄PF₆ result, under refluxing conditions, in the dissociation of one triphenylphosphine and the halide ligands to yield the monocationic complexes [(η⁵-C₅H₅)M(NnN)(PPh₃)]⁺ (1: M = Ru, NnN = 2-(2'-pyridyl)imidazole; 2: M = Ru, NnN = 2-(2'-pyridyl)benzimidazole; 3: M = Ru, NnN = 2-(2'-pyridyl)-4,5-dimethylimidazole; 4: M = Ru, NnN = 2-(2'-pyridyl)-4,5-diphenylimidazole; 5: M = Os, NnN = 2-(2'-pyridyl)imidazole; 6: M = Os, NnN = 2-(2'-pyridyl)benzimidazole), see Scheme 5.2. The compounds are isolated and characterized as hexafluorophosphate salts.
In the case of the reaction of the dinuclear iridium(III) complex \([(\eta^5-C_5Me_5)Ir(\mu-\text{Cl})\text{Cl}]_2\) with two equivalents of chelating \(\text{N} \cap \text{N}\) ligands in the presence of \(\text{NH}_4\text{PF}_6\), cleavage of the chloride-bridge followed by dissociation of one chloride ligand, affords the complexes \([(\eta^5-C_5Me_5)Ir\{2-(2'\text{-pyridyl})\text{imidazole}\}\text{Cl}]\text{PF}_6\) ([7]PF_6) and \([(\eta^5-C_5Me_5)Ir\{2-(2'\text{-pyridyl})\text{benzimidazole}\}\text{Cl}]\text{PF}_6\) ([8]PF_6), see Scheme 5.3.

The complexes (1-8) are pale yellow to orange reddish colored. They are highly soluble in polar solvents such as chloroform, acetone, methanol, dichloromethane etc., but insoluble in non-polar solvents such as hexane, pentane etc., C, H, N analyses, IR, \(^1\text{H}\)}
NMR spectroscopic data were given in the experimental section, which supported the formation of these complexes (1-8). The X-ray structures of representative complexes 1, 2 and 7 were determined to confirm the structure of the complexes (1-8).

Figure 5.1: Infrared spectrum of \( [(\eta^5-C_5Me_5)Ir\{2-(2'-pyridyl)imidazole\}Cl]PF_6 \) [7]

The infrared spectra of complexes (1-6) exhibited very strong bands at 1613-1600 cm\(^{-1}\) and 1480-1440 cm\(^{-1}\) corresponding to phenyl groups of triphenylphosphine and N-bases, while in complexes 7 and 8 prominent peaks were observed at 1600 cm\(^{-1}\) and 1474-1327 cm\(^{-1}\). The counter ion (PF\(_6\)) exhibit a strong band around 845 cm\(^{-1}\) for \( \nu_{PF} \) group (Figure 5.1). The protons' corresponding to the cyclopentadienyl ligands appear in the region of 4.6-4.7 ppm while the triphenylphosphine peaks are observed as multiplets in the aromatic region between 7-8 ppm. The chemical shifts of cyclopentadienyl groups are shifted to down field as compared to the precursor complexes (4.43-4.31 ppm) (Figure 5.2 and 5.3).
Figure 5.2: $^1$H NMR, $^{13}$C spectra of $[(\eta^5-C_5H_5)Ru\{2-(2'-pyridyl)benzimidazole(PPh_3)]PF_6[2]$

Figure 5.3: $^1$H and $^{31}$P {NMR}, spectra of $[(\eta^5-C_5H_5)Os\{2-(2'-pyridyl)benzimidazole\}$(PPh$_3$)]PF$_6$. 
Figure 5.4: \(^1\)H NMR, spectrum of \([(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}\{2-(2'\text{-pyridyl})benzimidazole\}]\text{Cl}\)PF\(_6\) [8]PF\(_6\).

The down field shift position of the cyclopentadienyl protons in complexes 1-6, which might result from the change in electron density on the metal center due to chelation of the nitrogen base ligands through the nitrogen atoms of the 2-(2'-pyridyl)imidazole derivatives ligands. The \(^1\)H NMR spectra of complexes 1-6 also showed two pseudo-triplets in the range of 7.85 - 6.32 ppm due to the pyridine protons (H\(_4\) and H\(_5\)) of the N\(\cap\)N-donor ligands. The spectra of the Cp\(^*\) complexes 7 and 8 showed resonance for the methyl protons of the Cp\(^*\) ligand as singlet at 1.86 ppm and 1.82 ppm respectively (Figure 5.4). Molecular structure of the representative hexafluorophosphates salts [1]PF\(_6\), [2]PF\(_6\) and [7]PF\(_6\) are presented in Figures 1, 2 and 4 respectively. Selected bond lengths and angles are recorded in Table 2. The molecular structures of \([(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{2-(2'\text{-pyridyl})imidazole\}\{(\text{PPh}_3)\}]^+\) (1) and \([(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{2-(2'\text{-pyridyl})benzimidazole\}\{(\text{PPh}_3)\}]^+\) (2) have been established by single-crystal X-ray structure analysis of [1]PF\(_6\) and [2]PF\(_6\)--- H\(_2\)O, respectively. Both complexes show typical piano-stool geometry with the metal center coordinated by a cyclopentadienyl ligand, a PPh\(_3\) ligand and a chelating N\(\cap\)N-ligand, see Figures 5.1 and 5.2.
Figure 5.5: ORTEP diagram with labelling scheme for \([(\eta^5-C_5H_5)Ru\{2-(2'-pyridyl)imidazole\}(PPh_3)]^+ (I)PF_6\), at 50\% probability level, H atoms and PF_6 anion omitted for clarity.

The Ru-N bond distances [2.113(3) and 2.093(3) Å in 1; 2.117(2) and 2.094(2) in 2] are comparable to those in \([(\eta^6-p-Pr\,C_6H_4Me)RuCl(2,3-bis(2-pyridyl)pyrazine)]BF_4 [17] and \([(\eta^6-C_6H_6)RuCl(2-(1-imidazole-2-yl)pyridine)]PF_6 [18a]. Accordingly, there is no significant difference in the Ru-P bond length in 1 [2.316(1) Å] or 2 [2.325(1) Å] with reported values [9d, 19]. The N(1)-Ru-N(3) bond angle in complexes 1 [76.0(1)°] and 2 [76.1(2)°] are similar to those of compounds \([(\eta^6-p-Pr\,C_6H_4Me)RuCl(2,3-bis(2-pyridyl)pyrazine)]^+ [N-Ru-N = 76.5(2)°] [17] and \([(\eta^6-p-Pr\,C_6H_4Me)RuCl(2,3-bis(2-pyridyl)quinoxaline)]^+ [N-Ru-N = 76.2(2)°] [18b]. The angles between the least-square
planes of $\eta^5$-C$_5$H$_5$ and that of the N$\equiv$N ligand are 57.8(2)$^\circ$ in 1 and 55.3(2)$^\circ$ in 2 (Table 5.2).

Figure 5.6: ORTEP diagram with labelling scheme for [(η5-C$_5$H$_5$)Ru{2-(2' -pyridyl)benzimidazole} (PPh$_3$)$_2$] ($[2]PF_6 \cdot H_2O$) at 50% probability level, H atoms, PF$_6$ anion and water molecule omitted for clarity.

Complex $[2]PF_6$ crystallizes with one molecule of water per asymmetric unit, which forms a hydrogen-bonded network with two hexafluorophosphate anions and the N-H group of the N$\equiv$N ligand, see Figure 3. The N-O and O-F distances of the hydrogen bonds are respectively, 2.820(3) Å for the N-H of the 2-(2'-pyridyl)benzimidazole ligand and H$_2$O, and 2.941(4) and 2.907(4) Å between the hexafluorophosphate anions and the water molecule (Table 5.2). The N-H···O angle is 167.1$^\circ$ while the O-H···F angles are 178 and 153$^\circ$, respectively.
The molecular structure of \([(\eta^5-C_5\text{Me}_5)\text{Ir}\{2-(2^\prime-\text{pyridyl})\text{imidazole}\}\text{Cl}]^+\) (7) has been established by single-crystal X-ray structure analysis of [7]PF$_6$ (see Figure 4). The complex shows a typical piano-stool geometry with the metal center coordinated by the pentamethylenecyclopentadienyl ligand, a terminal chloride and the 2-(2'-pyridyl)imidazole ligand. The Ir-N bond distances [2.106(5) and 2.080(5) Å] are slightly shorter than those in [1]PF$_6$ and [2]PF$_6$. The average distance between the metal atom and the carbon atoms of the \(\eta^5-C_5\text{Me}_5\) ring is 2.16 Å. This average bond length is comparable to that in the related \(\eta^5-C_5\text{Me}_5\) iridium complex \([(\eta^5-C_5\text{Me}_5)\text{IrCl(\text{1-phenylethylsalicylaldehyde})}]\) [2.17 Å] [20]. The Ir-Cl bond length is 2.4183(14) Å in 7, which is slightly longer than the reported iridium complex \([(\eta^5-C_5\text{Me}_5)\text{IrCl(\text{1-phenylethylsalicylaldehyde})}]\) [2.4017(16) Å] [20] (Table 5.2).
Figure 5.8: ORTEP diagram with labelling scheme for \([\eta^5-C_8Me_5]Ir\{2-(2'\text{-pyridyl})imidazole\}Cl\]^+ ([7]PF$_6$) at 50% probability level, H atoms and PF$_6$ anion omitted for clarity.

In the crystal packing of [7]PF$_6$, two molecules of 7 form a dimer through N-H--Cl contacts and \(\pi\)-stacking interactions, see Figure 5. The N--Cl separation is 3.254(5) Å with an N-H--Cl angle of 162.1°. The distance observed between the \(\pi\)-stacking interacting systems (centroid--centroid 3.76 Å) is in good agreement with the theoretical value calculated for this stacking mode [21]. The distance observed between the two iridium centres of the dimer is 7.841(1) Å and excludes any possible metal-metal interactions.
5.4. Conclusions:

The present study describe the syntheses of eight new ($\eta^5$-C$_5$H$_5$)Ru, ($\eta^5$-C$_5$H$_5$)Os and ($\eta^5$-C$_5$Me$_5$)Ir complexes containing 2-(2'-pyridyl)imidazole ligands. Representative complexes have been characterized by single X-ray study. In the crystal packing of [7]PF$_6$, two molecules of 7 form a dimer through N-H--Cl contacts and π-stacking interactions.

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<td>P 2₁/c (no. 14)</td>
<td>P -1 (no. 2)</td>
<td>P -1(no.2)</td>
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<tr>
<td>Crystal colour and shape</td>
<td>orange block</td>
<td>red block</td>
<td>red block</td>
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<tr>
<td>Crystal size</td>
<td>0.32 x 0.20 x 0.200</td>
<td>28 x 0.23 x 0.18</td>
<td>0.35 x 0.26 x 0.21</td>
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<tr>
<td>a (Å)</td>
<td>13.552(3)</td>
<td>10.379(4)</td>
<td>8.0428(9)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>14.582(3)</td>
<td>11.285(4)</td>
<td>11.4031(14)</td>
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<tr>
<td>c (Å)</td>
<td>17.920(6)</td>
<td>15.601(6)</td>
<td>11.7074(13)</td>
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<tr>
<td>α (°)</td>
<td>90</td>
<td>108.602(5)</td>
<td>93.585(14)</td>
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<td>β (°)</td>
<td>126.31(2)</td>
<td>91.211(5)</td>
<td>96.862(14)</td>
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<tr>
<td>γ (°)</td>
<td>90</td>
<td>104.887(5)</td>
<td>98.154(14)</td>
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<td>V (Å³)</td>
<td>2853.6(13)</td>
<td>1663.0(10)</td>
<td>1051.8(2)</td>
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<tr>
<td>Z</td>
<td>4</td>
<td>2</td>
<td>2</td>
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<tr>
<td>T (K)</td>
<td>173(2)</td>
<td>120(2)</td>
<td>173(2)</td>
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<tr>
<td>Dₑ (g.cm⁻³)</td>
<td>1.673</td>
<td>1.571</td>
<td>2.062</td>
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<tr>
<td>μ (mm⁻¹)</td>
<td>0.729</td>
<td>0.635</td>
<td>6.613</td>
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<td>Scan range (°)</td>
<td>1.86 &lt; θ &lt; 29.24</td>
<td>1.98 &lt; θ &lt; 28.23</td>
<td>2.58 &lt; θ &lt; 26.03</td>
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<tr>
<td>Unique reflections</td>
<td>6277</td>
<td>7437</td>
<td>3821</td>
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</tbody>
</table>
Chapter 5

Reflections used [I>2σ(I)] 4388 6379 3518

\( R_{int} \) 0.0588 0.0261 0.0501

Final R indices [I>2σ(I)]* 0.0387, wR_2 0.0860 0.0457, wR_2 0.1073 0.0323, wR_2 0.0782

R indices (all data) 0.0605, wR_2 0.0926 0.0543, wR_2 0.1131 0.0373, wR_2 0.0884

Goodness-of-fit 0.910 1.016 1.112

Max, Min Δρ/e (Å⁻³) 0.763, -1.038 0.754, -0.530 1.775, -1.850

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


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<th>Distances (Å)</th>
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<td>Ru-P</td>
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<td>2.325(1)</td>
<td>2.4183(14)</td>
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<td>Ir-Cl</td>
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<td>M-N1</td>
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<td>2.106(5)</td>
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<td>M-N3</td>
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<td>2.0939(15)</td>
<td>2.080(5)</td>
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<td>M-C1</td>
<td>2.208(4)</td>
<td>2.109(4)</td>
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<td>M-C2</td>
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<td>2.149(5)</td>
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<td>M-C3</td>
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<td>M-C4</td>
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<td>M-C5</td>
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<table>
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<th>Angles (°)</th>
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<tr>
<td>N1-M-N3</td>
<td>75.98(10)</td>
<td>76.08(17)</td>
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<td>N1-M-P1</td>
<td>90.12(8)</td>
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References


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