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which should be used for any reference to this work

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

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Abstract

The reaction of $[CpRu(PPh_3)_2Cl]$ and $[CpOs(PPh_3)_2Br]$ with chelating 2-(2′-pyridyl)imidazole (N ∩ N) ligands and NH_4PF_6 yields cationic complexes of the type $[CpM(N \cap N)(PPh_3)]^+$ (**1**: M = Ru, N ∩ N = 2-(2′-pyridyl)imidazole; **2**: M = Ru, N ∩ N = 2-(2′-pyridyl)benzimidazole; **3**: M = Ru, N ∩ N = 2-(2′-pyridyl)-4,5-dimethylimidazole; **4**: M = Ru, N ∩ N = 2-(2′-pyridyl)-4,5-diphenylimidazole; **5**: M = Os, N ∩ N = 2-(2′-pyridyl)imidazole; **6**: M = Os, N ∩ N = 2-(2′-pyridyl)benzimidazole). They have been isolated and characterized as their hexafluorophosphate salts. Similarly, in the presence of NH_4PF_6, $[Cp*Ir(\mu\text{-}Cl)Cl]_2$ reacts in dry methanol with N ∩ N chelating ligands to afford in excellent yield $[Cp*Ir(N \cap N)Cl]PF_6$ (**7**: N ∩ N = 2-(2′-pyridyl)imidazole; **8**: N ∩ 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.

Keywords: Cyclopentadienyl; Pentamethylcyclopentadienyl; Ruthenium; Osmium; Iridium; 2-(2′-Pyridyl)imidazole

1. Introduction

The chemistry of cyclopentadienyl bisphosphine ruthenium complexes $[CpRu(PPh_3)_2X]$ 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 $[CpOs(PPh_3)_2Br]$ chemistry have not been studied extensively due to lower kinetic liability 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 N ∩ N-donor bases [6]. The chemistry of $[CpRu(PPh_3)_2Cl]$ 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 vinyllidines and allenylidines [8]. We had reported that the reactions of cyclopentadienyl ruthenium(II), $[Cp*Ru(PPh_3)_2(CH_3CN)]^+$ and $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2(CH_3CN)]^+$ [9] with a variety of nitrogen based ligands.

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In this paper, as a part of our continuing study, we would like to report the synthesis and characterization of new cationic cyclopentadienyl (Cp) ruthenium(II), osmium(II) and pentamethylcyclopentadienyl (Cp*) iridium(III) complexes with chelating N ∩ N-donor ligands [L_1 = 2-(2′-pyridyl)imidazole, L_2 = 2-(2′-pyridyl)benzimidazole, L_3 = 2-(2′-pyridyl)-4,5-dimethylimidazole, L_4 = 2-(2′-pyridyl)-4,5-diphenylimidazole (Scheme 1). In order to confirm the nature of bonding, the molecular structures of [CpRu{2-(2′-pyridyl)imidazole}(PPh_3)]PF_6 ([**1**]PF_6), [CpRu{2-(2′-pyridyl)benzimidazole}(PPh_3)]PF_6 ([**2**]PF_6) and [Cp*Ir{2-(2′-pyridyl)imidazole}Cl] PF_6 ([**7**]PF_6) have been solved by X-ray crystallography.

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 [$CpRu(PPh_3)_2Cl$], [$CpOs(PPh_3)_2Br$] [11] and [Cp*Ir(μ-Cl)Cl]$_2$ [12] were prepared by following the reported literature methods.

2.1. Synthesis of [CpRu(N ∩ N)(PPh$_3$)]PF$_6$

The following general procedure was used for the preparation of complexes [**1**]PF_6 to [**4**]PF_6.

2.1.1. Preparation of [1]PF$_6$

A mixture of [$CpRu(PPh_3)_2Cl$] (0.1 g, 0.14 mmols), 2-(2′-pyridyl)imidazole (0.04 g, 0.28 mmols) and NH_4PF_6 (0.046 g, 0.28 mmols) was refluxed in dry methanol (20 ml) under a nitrogen atmosphere for 6 h. The yellow suspension turns to a light yellow color. The solvent is evaporated at reduced pressure. Then the residue is dissolved in dichloromethane (5 ml), and the solution filtered to remove ammonium chloride. The yellow solution is 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**]PF_6.

Complex [CpRu{2-(2′-pyridyl)imidazole}(PPh_3)]PF_6 [**1**]PF_6 (Yield: 63 mg, 64%). Elemental *Anal.* Calc. for $C_{31}H_{27}N_3F_6P_2Ru$: 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 ($\nu_{C=C}$), 1480, 1440 ($\nu_{C=N}$), 857 (ν_{PF6}), ^{1}H NMR ($CDCl_3$, δ): 12.01 (s, 1H, NH); 9.04 (d, J_{H-H} = 5.74 Hz, 1H, H_6); 8. 75 (d, J_{H-H} = 6.08 Hz, H_7); 8.50 (d, J_{H-H} = 6.02 Hz, H_8); 8.00 (d, J_{H-H} = 5.12 Hz, 1H, H_3); 7.78 (m, 15H, Ph); 7.70 (t, 1H, H_4); 7.32 (t, 1H, H_5); 4.68 (s, 5H, C_5H_5).

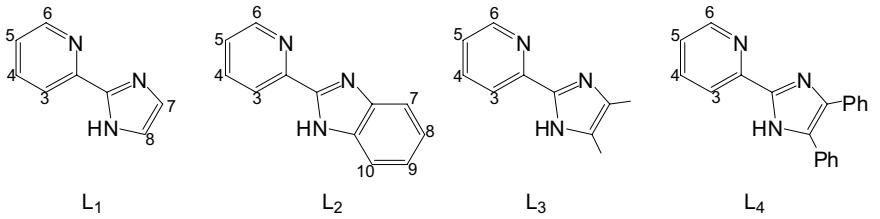
Complex [CpRu{2-(2′-pyridyl)benzimidazole}(PPh_3)]-PF_6 [**2**]PF_6 (Yield: 65 mg, 62%). Elemental *Anal.* Calc. for $C_{35}H_{29}F_6P_2N_3Ru$: C, 54.69; H, 3.78; N, 5.47. Found: C, 54.87; H, 4.12; N, 5.67%. IR (KBr pellets, cm^{-1}): 1613 ($\nu_{C=C}$), 1447 ($\nu_{C=N}$), 850 (ν_{PF6}), ^{1}H NMR ($CDCl_3$, δ): 12.01 (s, 1H, NH); 8.94 (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_5H_5).

Complex [CpRu{2-(2′-pyridyl)-4,5-dimethylimidazole}-(PPh_3)]PF_6 [**3**]PF_6 (Yield: 64 mg, 62%). Elemental *Anal.* Calc. for $C_{33}H_{31}F_6P_2N_3Ru$: 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 (ν_{P-F}), ^{1}H NMR ($CDCl_3$, δ): 12.10 (s, 1H, NH); 8.50 (d, J_{H-H} = 5.74 Hz, 1H, H_6); 8.18 (d, J_{H-H} = 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_5H_5); 3.21 (s, 6H, CH_3).

Complex [CpRu{2-(2′-pyridyl)-4,5-diphenylimidazole}-(PPh_3)]PF_6 [**4**]PF_6 (Yield: 70 mg, 60%). Elemental *Anal.* Calc. for $C_{43}H_{35}N_3P_2F_6Ru$: 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 (ν_{P-F}), ^{1}H NMR ($CDCl_3$, δ): 8.50 (d, J_{H-H} = 5.0 Hz, 1H, H_6); 8.27 (d, J_{H-H} = 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_5H_5).

2.2. Synthesis of [CpM(N ∩ N)(PPh$_3$)]PF$_6$

These complexes were prepared by the same method given in Section 2.1 using of [$CpOs(PPh_3)_2(CH_3CN)$]PF_6 instead of [$CpRu(PPh_3)_2Cl$].



Scheme 1. Ligands and numbering scheme used in this study.

Complex [CpOs{2-(2′-pyridyl)imidazole}(PPh_3)]PF_6 [**5**]PF_6 (Yield: 48 mg, 57%). Elemental *Anal.* Calc. for $C_{31}H_{27}N_3P_2F_6Os$: 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 ($\nu_{C=C}$), 1480, 1440 (s, $\nu_{C=N}$), 885 (s, br, ν_{PF6}) ^1H NMR ($CDCl_3$, δ): 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_5H_5).

Complex [CpOs{2-(2′-pyridyl)benzimidazole}(PPh_3)]-PF_6 [**6**]PF_6 (Yield: 46 mg, 52%). Elemental *Anal.* Calc. for $C_{35}H_{29}N_3P_2F_6Os$: 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 ($\nu_{C=C}$), 1447 ($\nu_{C=N}$), 885 (s, br, ν_{PF6}). ^1H (NMR, $CDCl_3$, δ): 8.50 (d, $J_{H-H} = 5.2$ Hz, 1H, H_6); 8.10 (d, $J_{H-H} = 5.2$ Hz, 1H, H_3); 7.93 (m, 15H, Ph); 7.78 (t, 1H, H_4); 7.56 (t, 1H, H_5); 7.37 (m, 4H H_{7-10}); 4.65 (s, 5H, C_5H_5).

2.3. Synthesis of [Cp*Ir(N ∩ N)Cl]PF_6

These complexes were prepared by the same method given in Section 2.1 using 0.5 equiv. of [Cp*Ir(μ-Cl)Cl]$_2$ instead of 1 equiv. of [CpM(PPh_3)$_2$Cl].

Complex [Cp*Ir{2-(2′-pyridyl)imidazole}Cl]PF_6 [**7**]PF_6 (Yield: 52 mg, 64%). Elemental *Anal.* Calc. for $C_{18}H_{22}ClN_3F_6PIr$: 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 ($\nu_{C=C}$), 1460–1327 ($\nu_{C=N}$), 850 (ν_{P-F}), ^1H 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); 1.86 (s, 15H, C_5Me_5).

Complex [Cp*Ir{2-(2′-pyridyl)benzimidazole}Cl]PF_6 [**8**]PF_6 (Yield: 54 mg, 62%). Elemental *Anal.* Calc. for $C_{22}H_{24}ClN_3F_6PIr$: 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 ($\nu_{C=C}$), 1474–1407 ($\nu_{C=N}$), 850 (ν_{P-F}), ^1H 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_{7-10}); 1.82 (s, 15H, C_5Me_5).

2.4. Single-crystal X-ray structures analyses

Crystal suitable for X-ray diffraction study for compound [**1**]PF_6, [**2**]PF_6 and [**7**]PF_6 were grown by slow diffusion of diethylether into dichloromethane solution of complexes [**1**]PF_6, [**2**]PF_6 and [**7**]PF_6, respectively. The orange reddish crystals of compound [**1**]PF_6 and [**7**]PF_6 were mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, using Mo Kα graphite monochromated radiation ($\lambda = 0.71073$ Å) with ϕ range 0–200°, increment of 1.2°, D_{max}–$D_{min} = 12.45$–0.81 Å. Whereas crystal of [**2**]PF_6 was mounted on a Bruker Apex CCD diffractometer in a full 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**]$PF_6 \cdot H_2O$, the $-C_5H_4NC_3N_2H-$ 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. Figs. 1, 2 and 4 are drawn with ORTEP32 [15] while Figs. 3 and 5 are drawn with MERCURY [16].

3. Results and discussion

The reactions in dry methanol of [CpRu(PPh_3)$_2$Cl] and [CpOs(PPh_3)$_2$Br] (Cp = η^5-C_5H_5) with an excess of chelating N ∩ N-ligands and NH_4PF_6 result, under refluxing conditions, in the dissociation of one triphenylphosphine and the halide ligands to yield the monocationic complexes [CpM(N ∩ N)(PPh_3)]$^+$ (**1**: M = Ru, N ∩ N = 2-(2′-pyridyl) imidazole; **2**: M = Ru, N ∩ N = 2-(2′-pyridyl)benzimidazole; **3**: M = Ru, N ∩ N = 2-(2′-pyridyl)-4,5-dimethylimidazole; **4**: M = Ru, N ∩ N = 2-(2′-pyridyl)-4,5-diphenylimidazole; **5**: M = Os, N ∩ N = 2-(2′-pyridyl)imidazole; **6**: M = Os, N ∩ N = 2-(2′-pyridyl)benzimidazole), see Scheme 2. The compounds are isolated and characterized as hexafluorophosphate salts.

In the case of the reaction of the dinuclear iridium(III) complex [Cp*Ir(μ-Cl)Cl]$_2$ (Cp = η^5-C_5Me_5) with 2 equiv. of chelating N ∩ N-ligands in the presence of NH_4PF_6, cleavage of the chloro-bridge followed by dissociation of one chloride ligand, affords the complexes [Cp*Ir{2-(2′-pyridyl)imidazole}Cl]PF_6([**7**]PF_6) and [Cp*Ir{2-(2′-pyridyl)benzimidazole}Cl]PF_6 ([**8**]PF_6), see Scheme 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, ^1H NMR spectroscopic data were given in the experimental section, which supported the formation of these complexes. The X-ray structures of representative complexes **1**, **2** and **7** were determined to confirm the structure of the complexes (**1–8**). 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 ν_{PF6} group.

The protons' corresponding to the cyclopentadienyl ligands appear in the region of 4.6–4.7 ppm while the triphenylphosphine peaks are observed as a multiplet in the aromatic region between 7 and 8 ppm. The chemical shifts of cyclopentadienyl groups appear downfield as compared

Table 1
Crystallographic and structure refinement parameters for complexes [**1**]PF_6, [**2**]$PF_6 \cdot H_2O$ and [**7**]PF_6

	[**1**]PF_6	[**2**]$PF_6 \cdot H_2O$	[**7**]PF_6
Chemical formula	$C_{31}H_{27}F_6N_3P_2Ru$	$C_{35}H_{31}F_6N_3OP_2Ru$	$C_{18}H_{22}ClF_6N_3PIr$
Formula weight	718.57	786.64	653.01
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
Crystal colour and shape	orange block	red block	red block
Crystal size	$0.32 \times 0.20 \times 0.20$	$0.28 \times 0.23 \times 0.18$	$0.35 \times 0.26 \times 0.21$
a (Å)	13.552(3)	10.379(4)	8.0428(9)
b (Å)	14.582(3)	11.285(4)	11.4031(14)
c (Å)	17.920(6)	15.601(6)	11.7074(13)
α (°)	90	108.602(5)	93.585(14)
β (°)	126.31(2)	91.211(5)	96.862(14)
γ (°)	90	104.887(5)	98.154(14)
V (Å^3)	2853.6(13)	1663.0(10)	1051.8(2)
Z	4	2	2
T (K)	173(2)	120(2)	173(2)
D_c (g cm^{-3})	1.673	1.571	2.062
μ (mm^{-1})	0.729	0.635	6.613
Scan range (°)	$1.86 < \theta < 29.24$	$1.98 < \theta < 28.23$	$2.58 < \theta < 26.03$
Unique reflections	6277	7437	3821
Reflections used [$I > 2\sigma(I)$]	4388	6379	3518
R_{int}	0.0588	0.0261	0.0501
Final R indices [$I > 2\sigma(I)$][a]	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
Maximum and minimum $\Delta\rho$ (e Å^{-3})	0.763, −1.038	0.754, −0.530	1.775, −1.850

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

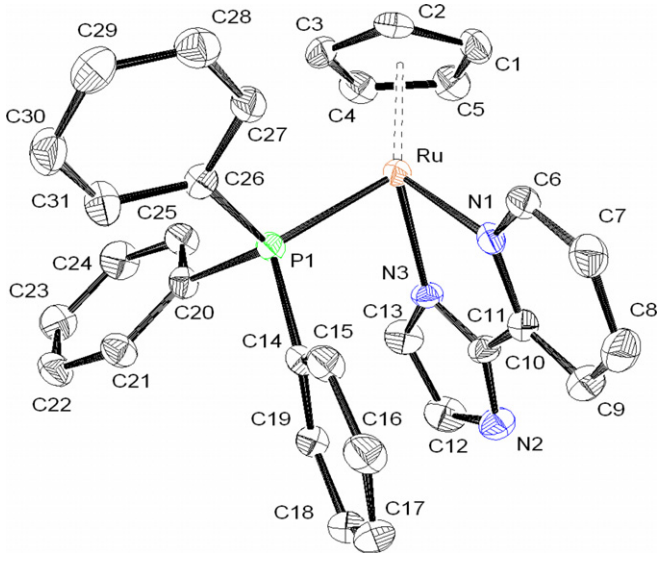


Fig. 1. ORTEP diagram with labelling scheme for [CpRu{2-(2′-pyridyl)imidazole}(PPh_3)]$^+$ ([**1**]PF_6), at 50% probability level, H-atoms and PF_6 anion omitted for clarity.

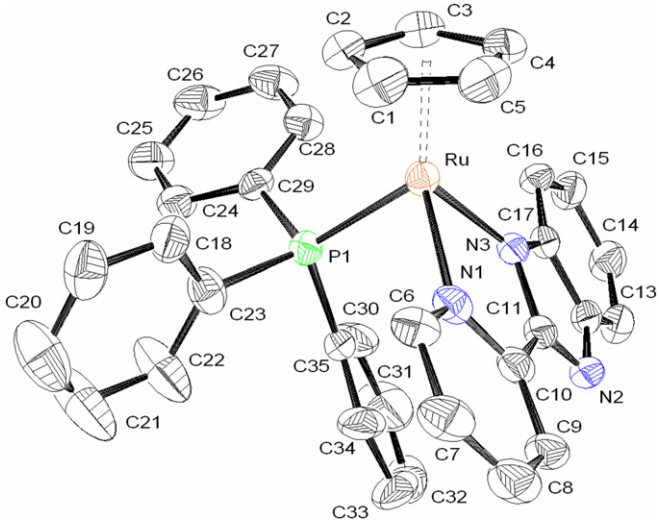


Fig. 2. ORTEP diagram with labelling scheme for [CpRu{2-(2′-pyridyl)benzimidazole}(PPh_3)]$^+$ ([**2**]$PF_6 \cdot H_2O$) at 50% probability level, H-atoms, PF_6 anion and water molecule omitted for clarity.

to the precursor complexes (4.43–4.31 ppm). The downfield shift position of the cyclopentadienyl protons in complexes **1–6**, which might results 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 (H4 and H5) of the N ∩ N-donor ligands, a singlet at 12.01 ppm corresponds to the NH protons of the ligands. The spectra of the Cp* complexes **7** and **8** showed resonance for the methyl protons of the Cp* ligand as singlets at 1.86 ppm and 1.82 ppm, respectively.

Molecular structure of the representative hexafluorophosphates salts [**1**]PF_6, [**2**]PF_6 and [**7**]PF_6 are presented in Figs. 1, 2 and 4, respectively. Selected bond lengths and angles are recorded in Table 2. The molecular

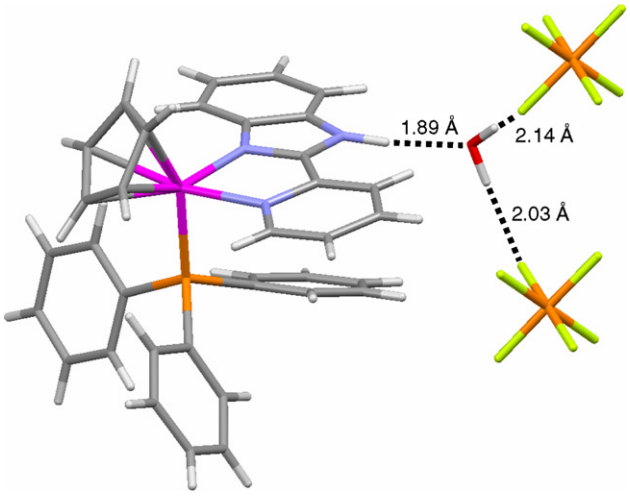
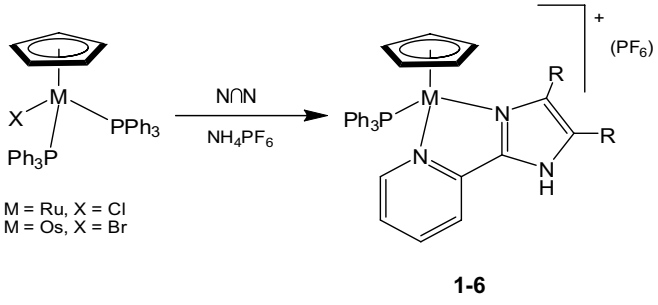
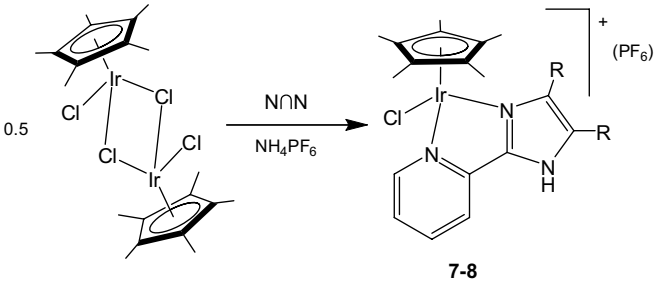


Fig. 3. Hydrogen-bonded system observed in [**2**]$PF_6 \cdot H_2O$.



Scheme 2.



Scheme 3.

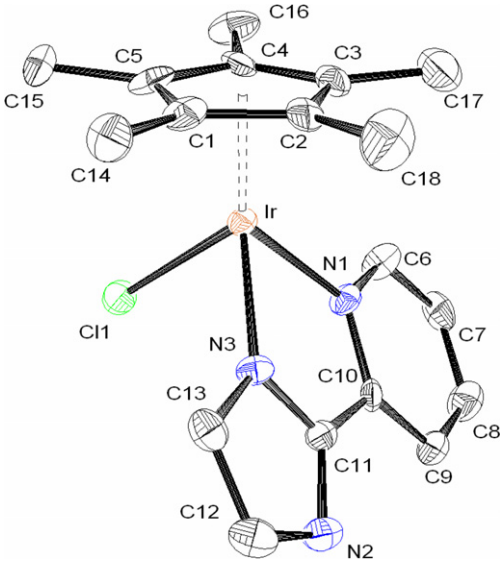


Fig. 4. ORTEP diagram with labelling scheme for [Cp*Ir{2-(2′-pyridyl)imidazole}Cl]$^+$ ([**7**]PF_6) at 50% probability level, H-atoms and PF_6 anion omitted for clarity.

Table 2
Selected bond lengths and angles for complexes [**1**]PF_6, [**2**]$PF_6 \cdot H_2O$ and [**7**]PF_6

	1	**2**	**7**
Distances (Å)			
Ru–P	2.316(1)	2.325(1)	
Ir–Cl			2.4183(14)
M–N1	2.113(3)	2.1169(17)	2.106(5)
M–N3	2.093(3)	2.0939(15)	2.080(5)
M–C1	2.208(4)	2.109(4)	2.178(6)
M–C2	2.177(4)	2.157(3)	2.149(5)
M–C3	2.150(4)	2.226(3)	2.158(6)
M–C4	2.180(4)	2.219(3)	2.144(6)
M–C5	2.215(4)	2.146(4)	2.164(6)
Angles (°)			
N1–M–N3	75.98(10)	76.08(17)	76.48(19)
N1–M–P1	90.12(8)	92.15(6)	
N3–M–P1	87.66(8)	89.02(6)	
N1–Ir–Cl1			84.60(14)
N3–Ir–Cl1			86.95(14)

structures of [CpRu{2-(2′-pyridyl)imidazole}(PPh_3)]$^+$ (**1**) and [CpRu{2-(2′-pyridyl)benzimidazole}(PPh_3)]$^+$ (**2**) have been established by single-crystal X-ray structure analysis of [**1**]PF_6 and [**2**]$PF_6 \cdots H_2O$, 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 ∩ N-ligand, see Figs. 1 and 2.

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 [(η^6-*p*-Pr^{i}C$_6$H$_4$Me)RuCl(2,3-bis(2-pyridyl)pyrazine)]-BF_4[17] and [(η_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 [(η^6-*p*-Pr^{i}C$_6$H$_4$-Me)RuCl(2,3-bis(2-pyridyl)pyrazine)]$^+$ [N–Ru–N = 76.5 (2)°] [17] and [(η^6-*p*-Pr^{i}C$_6$H$_4$Me)RuCl(2,3-bis(α-pyridyl)quinoxaline)]$^+$ [N–Ru–N = 76.2(2)°] [18b]. The angles between the least-square planes of η^5-C_5H_5 and that of the N ∩ N-ligand are 57.8(2)° in **1** and 55.3(2)° in **2**.

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 ∩ N ligand, see Fig. 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

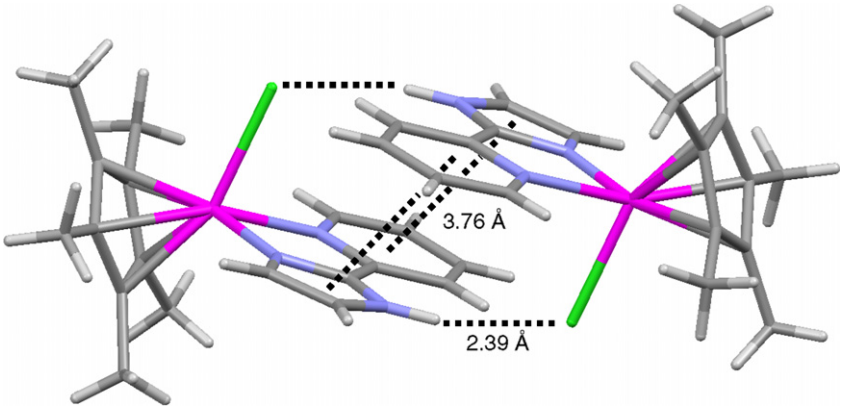


Fig. 5. Dimeric structure of [**7**]PF_6 showing the intermolecular NH···Cl hydrogen contacts and π–π interacting system.

ligand and H_2O, and 2.941(4) and 2.907(4) Å between the hexafluorophosphate anions and the water molecule. The N–H···O angle is 167.1° while the O–H···F angles are 178° and 153°, respectively.

The molecular structure of [Cp*Ir{2-(2′-pyridyl)imidazole}Cl]$^+$ (**7**) has been established by single-crystal X-ray structure analysis of [**7**]PF_6 (see Fig. 4). The complex shows a typical piano-stool geometry with the metal center coordinated by the pentamethylcyclopentadienyl 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 to those in [**1**]PF_6 and [**2**]PF_6. The average distance between the metal atom and the carbon atoms of the η^5-C_5Me_5 ring is 2.16 Å. This average bond length is comparable to that in the related η^5-C_5Me_5 iridium complex [(η^5-C_5Me_5)IrCl((*S*)-1-phenylethylsalicylaldiimine)] [2.17 Å] [20]. The Ir–Cl bond length is 2.4183(14) Å in **7**, which is slightly longer to the reported iridium complex [(η^5-C_5Me_5)IrCl((*S*)-1-phenylethylsalicylaldiimine)] [2.4017(16) Å] [20].

In the crystal packing of [**7**]PF_6, two molecules of **7** form a dimer through N–H···Cl contacts and π-stacking interactions, see Fig. 5. The N–Cl separation is 3.254(5) Å with an N–H···Cl angle of 162.1°. The distance observed between the π-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 centers of the dimer is 7.841(1) Å and excludes any possible metal–metal interactions.

4. Conclusions

The present study describes the synthesis of eight new CpRu, CpOs and Cp*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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Appendix A. Supplementary material

CCDC 637370, 637371 and 637372 contain the supplementary crystallographic data for [**1**]PF_6, [**2**]$PF_6 \cdot H_2O$ and [**7**]PF_6. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.03.055.

References

[1] (a) W. Baratta, E. Herdtweck, W.A. Hermann, P. Rigo, J. Schwarz, Organometallics 21 (2002) 2101;
(b) M.A. Bennett, K. Khan, E. Wenger, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry II, second ed., vol. 7, Elsevier, Oxford, 1995, Chapter 8 and references cited therein.

[2] (a) S.G. Davies, J.P. McNally, J. Smallridge, Adv. Organomet. Chem. 30 (1991) 1;
(b) B.M. Trost, J.A. Marting, R.J. Kulawiec, A.F. Indolese, J. Am. Chem. Soc. 115 (1993) 10402;
(c) P. Pertici, V. Ballantini, P. Salvadori, M.A. Bennett, Organometallics 14 (1995) 2565;
(d) D.L. Davies, J. Fawcett, R. Krafczyk, D.R. Russell, J. Organomet. Chem. 545–546 (1997) 581.

[3] (a) B.M. Trost, M.U. Frederiksen, M.T. Rudd, Angew. Chem., Int. Ed. Eng. 44 (2005) 6630, and references cited therein;
(b) W. Baratta, A.D. Zotto, P. Rigo, Chem. Commun. (1997) 2163;
(c) A.D. Zotto, W. Baratta, G. Verardo, P. Rigo, Eur. J. Org. Chem. (2000) 2795.

[4] M.A. Esteruelas, E.G. Puebla, A.M. López, E. Oñate, J.I. Tolosa, Organometallics 19 (2000) 275.

[5] (a) R. Lalrempuia, H. Yennawar, Y.A. Mozharivskyj, K. Mohan Rao, J. Organomet. Chem. 689 (2004) 539;
(b) T. Wilczewski, J. Organomet. Chem. 317 (1986) 307;
(c) T. Wilczewski, J. Organomet. Chem. 297 (1985) 331;
(d) M.I. Bruce, G.A. Koutsantonis, M.J. Liddel, B.K. Nicholson, J. Organomet. Chem. 320 (1987) 217, and references cited therein.
[6] (a) P. Govindaswamy, K. Mohan Rao, J. Coord. Chem. 59 (2006) 663;
(b) P. Govindaswamy, Y.A. Mozharivskyj, K. Mohan Rao, Polyhedron 24 (2005) 1710;
(c) H. Aneetha, P.S. Zacharias, B. Srinivas, G.H. Lee, Y. Wang, Polyhedron 18 (1999) 299.
[7] (a) T. Blackmore, M.I. Bruce, F.G.A. Stone, J. Chem. Soc. A (1971) 2376;
(b) G.S. Ashby, M.I. Bruce, I.B. Tomkins, R.C. Wallis, Aust. J. Chem. 32 (1979) 1003;
(c) S.G. Davies, S.J. Simpson, H. Felkin, T. Fillebeen-Khan, Organometallics 2 (1983) 539;
(d) S.G. Davies, S.J. Simpson, H. Felkin, T. Fillebeen-Khan, F. Tadjand, O. Watts, J. Chem. Soc., Chem. Commun. (1981) 341;
(e) M.I. Bruce, S.F. Wong, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (1981) 1398.
[8] (a) J.P. Selegue, Organometallics 1 (1982) 217;
(b) J.P. Selegue, J. Am. Chem. Soc. 105 (1983) 5921.
[9] (a) R. Lalrempuia, P. Govindaswamy, Y.A. Mozharivskyj, K. Mohan Rao, Polyhedron 23 (2004) 1069;
(b) K. Mohan Rao, E.K. Rymmai, Polyhedron 22 (2003) 307;
(c) K. Sarjit Singh, P.J. Carroll, K. Mohan Rao, Polyhedron 24 (2005) 391;
(d) K. Sarjit Singh, Y.A. Mozharivskyj, C. Thone, K. Mohan Rao, J. Organomet. Chem. 690 (2005) 3720.
[10] B. Chiswell, F. Lions, B.S. Morris, Inorg. Chem. 31 (1964) 110.
[11] (a) M.I. Bruce, N.J. Windsor, Aust. J. Chem. 30 (1977) 1601;
(b) M.I. Bruce, P.J. Low, B.W. Skelton, E.R.T. Tiekink, A. Werth, A.H. White, Aust. J. Chem. 48 (1995) 1887.
[12] (a) J.W. Kang, K. Moseley, P.M. Maitlis, J. Am. Chem. Soc. 91 (1969) 5970;
(b) C. White, A. Yates, P.M. Maitlis, Inorg. Synth. 29 (1992) 228.
[13] M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.
[14] M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen, Germany, 1999.
[15] L.J. Farrugia, J. Appl. Cryst. 30 (1997) 565.
[16] I.J. Bruno, J.C. Cole, P.R. Edgington, M. Kessler, C.F. Macrae, P. Mc Cabe, J. Pearson, R. Taylor, Acta Crystallogr., Sect. B 58 (2002) 389.
[17] A. Singh, N. Singh, D.S. Pandey, J. Organomet. Chem. 642 (2002) 48.
[18] (a) H. Mishra, R. Mukherjee, J. Organomet. Chem 691 (2006) 3545;
(b) R. Lalrempuia, K. Mohan Rao, Polyhedron 22 (2003) 3155.
[19] P. Govindaswamy, C. Sinha, K. Mohan Rao, J. Organomet. Chem. 690 (2005) 3465.
[20] H. Brunner, A. Köllnberger, T. Burgemeister, M. Zabel, Polyhedron 19 (2000) 1519.
[21] S. Tsuzuki, K. Honda, T. Uchimura, M. Mikami, K. Tanabe, J. Am. Chem. Soc. 124 (2002) 104.