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New pentamethylcyclopentadienyl rhodium and iridium complexes containing arylazoimidazole ligands: Crystal and molecular structure of the complex $[(\eta^5\text{-}C_5Me_5)RhCl(Me\text{–}C_6H_4\text{–}N{=}N\text{–}C_3H_3N_2)]^+$

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Abstract

The dimeric $[\{(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl\}_2]$ complexes ($\eta^5\text{-}C_5Me_5$ = pentamethylcyclopentadienyl; M = Rh and Ir) react with several arylazoimidazole (RaaiR′) ligands, *viz*., 2-(phenylazo)imidazole (Phai-H), 1-methyl-2-(phenylazo)imidazole (Phai-Me), 1-ethyl-2-(phenylazo)imidazole (Phai-Et), 2-(tolylazo)imidazole (Tai-H), 1-methyl-2-(tolylazo)imidazole (Tai-Me) and 1-ethyl-2-(tolylazo)imidazole (Tai-Et), to afford complexes of the type $[(\eta^5\text{-}C_5Me_5)MCl(RaaiR')]^+$ where M = Rh or Ir; R, R′ = H (**1**, **7**), R = H, R′ = CH_3 (**2**, **8**), R = H, R′ = C_2H_5 (**3**, **9**), R = CH_3, R′ = H (**4**, **10**), R, R′ = CH_3 (**5**, **11**), R = CH_3, R′ = C_2H_5 (**6**, **12**), respectively. These complexes have been characterized by FT IR, FT NMR spectroscopy as well as by analytical data. The molecular structure of the hexafluorophosphate salt of the complex $[(\eta^5\text{-}C_5Me_5)RhCl(Me\text{–}C_6H_4\text{–}N{=}N\text{–}C_3H_3N_2)]^+$ **4**$[PF_6]$ has been established by single crystal X-ray diffraction study.

Keywords: Pentamethylcyclopentadienyl; Arylazoimidazole; Rhodium; Iridium

1. Introduction

The dimeric chloro bridged complexes $[\{(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl\}_2]$ (M = Rh or Ir) have been the subject of investigation by many research groups as these are very useful starting materials [1]. The complexes undergo rich variety of chemistry via the intermediacy of chloro bridge cleavage reactions leading to the formation of series of interesting neutral and cationic mononuclear complexes [2]. Despite extensive studies on the complex $[\{(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl\}_2]$, its reactivity with arylazoimidazole ligands (RaaiR′) are yet to be explored. Recently, the design of molecular architectures with imidazole ligands has contributed to the understanding of biomolecular interactions with metal ions in biology and provides models for the active sites of metalloproteins [3–6]. The molecule bears the azoimine (–N=N–C=N–) functional group, and is an efficient π-acid system for the stabilization of low oxidation state metal ions. The chemistry of this functional group with platinum is also known in detail [7–9]. The ligands used in the present study are shown in Scheme 1.

We had reported previously the synthesis of cyclopentadienyl and arene-ruthenium complexes containing N,N-donor arylazoimidazole ligands [10]. We also reported

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[1] X-ray crystallography.

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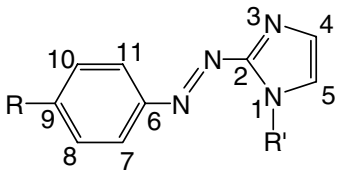
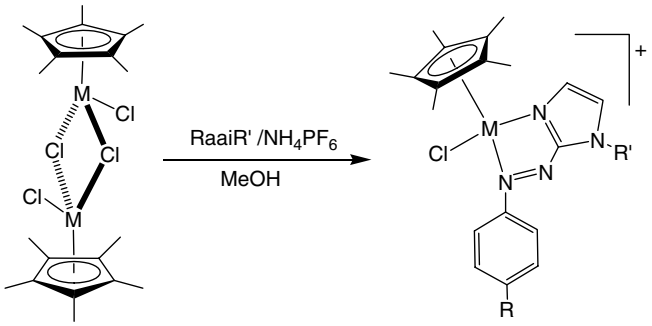


R, R' = H (Pai-H)
R, R' = H, CH_3 (Phai-Me)
R, R' = H, C_2H_5 (Phai-Et)
R, R' = CH_3, H (Tai-H)
R, R' = CH_3 (Tai-Me)
R, R' = CH_3, C_2H_5

Scheme 1.



M = Rh, Ir

R, R' = H; M = Rh (**1**), M = Ir (**7**)
R, R' = H, CH_3; M = Rh (**2**), M = Ir (**8**)
R, R' = H, C_2H_5; M = Rh (**3**), M = Ir (**9**)
R, R' = CH_3, H; M = Rh (**4**), M = Ir (**10**)
R, R' = CH_3; M = Rh (**5**), M = Ir (**11**)
R, R' = CH_3, C_2H_5; M = Rh (**6**), M Ir (**12**)

Scheme 2.

synthesis of cyclopentadienyl ruthenium [11], indenyl-ruthenium [12] and arene-ruthenium [13] complexes with a variety of nitrogen-based ligands. However, the analogous pentamethylcyclopentadienyl rhodium(III) and iridium(III) azo complexes have not been explored as much as the corresponding isoelectronic cyclopentadienyl and arene-ruthenium(II) complexes. As a part of our continuing study, we would like to report herein the syntheses and characterization of new cationic pentamethylcyclopentadienyl rhodium(III) and iridium(III) complexes with N,N-donor arylazoimidazole ligands.

2. Results and discussion

1-Methyl-2-(arylazo)imidazole (aai-Me), 1-ethyl-2-(arylazo)imidazole (aai-Et) and 2-(arylazo)imidazole (aai-H) were synthesized by coupling the aryldiazonium ions with imidazole in aqueous sodium carbonate solution (pH 7) and purified by the reported method [26]. The alkylation was carried out by adding alkyl halide in dry THF solution to the corresponding 2-(arylazo)imidazole in the presence of sodium hydride [14].

Six arylazoimidazole (RaaiR′) (see Scheme 1) ligands have been used in this work. Ligands are unsymmetrical N,N′-bidentate chelates, where N and N′ abbreviated to N (imidazole) and N′ (azo) donor centers, respectively. The pentamethylcyclopentadienyl rhodium and iridium dimers $[\{(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl\}_2]$ where M = Rh and Ir reacted with arylazoimidazoles (RaaiR′) in the presence of ammonium salts in methanol to form mononuclear cationic complexes having the general formula $[(\eta^5\text{-}C_5Me_5)MCl(RaaiR')]^+$ (C_5Me_5 = pentamethylcyclopentadienyl; M = Rh or Ir) (Scheme 2). The cationic complexes **1**–**6** are orange, while the complexes **7**–**12** are brown in colour. These complexes are non-hygroscopic, air-stable, shiny crystalline solids. They are sparingly soluble in methanol and benzene, soluble in dichloromethane, chloroform, acetone, acetonitrile, and insoluble in hexane, petroleum ether and diethyl ether.

The analytical data of these complexes are consistent with the formulations (Table 1). The formation of cationic complexes **1**–**6** and **7**–**12** are confirmed by the appearance of the strong band at around 840 cm^{-1} due to the $\nu_{(P-F)}$ of the PF_6^- anion. The bands appearing at around 1600 and 1400 cm^{-1} are assigned for $\nu_{(C=N)}$ and $\nu_{(N=N)}$, respectively, of the ligand [15].

The ^1H NMR spectrum of complexes shows a singlet for the pentamethylcyclopentadienyl protons in the range 1.38–1.71 ppm, indicating downfield shift from the starting dimeric complexes. A downfield shift in the position of the pentamethylcyclopentadienyl protons might result from a change in electron density on the metal center due to chelation of the arylazoimidazole ligand through its nitrogen atoms. The N–H proton of complexes **1**, **4**, **7** and **10** is exhibited a singlet in the range 8.2–9.2 ppm. The N-methyl protons (N-Me) of complexes **2**, **5**, **8** and **11** appear as a singlet at 3.82–4.19 ppm. The N-methylene proton (N-CH_2) of complexes **3**, **6**, **9** and **12** appears as a quartet in the range 4.14–4.55 ppm. All these complexes show doublet and multiplet in the range of 5.75–7.96 ppm due to the phenyl protons of the azoimine ligand.

The ^{31}C $\{^1H\}$ NMR spectrum of complexes **1**–**6** and **7**–**12** contain resonances for the pentamethylcyclopentadienyl ring carbons at around 90 ppm. The resonance observed at 155 ppm may be due to the azoimine (C=N) carbon of the ligand. The spectra also show resonances in the range of 122.1–162.2 ppm for the aromatic carbons and carbons of imidazole C–H group.

2.1. Electronic spectra

The low spin d^6 configuration of the mononuclear complexes provides filled orbitals of proper symmetry, which can interact with low lying π^* orbitals of the arylazoimidazole ligands (RaaiR′). A band attributable to the MLCT ($t_{2g} \rightarrow \pi^*$) transition is therefore expected in the electronic spectra [16], where the transition energy of these bands varies with the nature of the ligands acting as π-acceptors. The presence of electron donating groups (H, CH_3, C_2H_5) on the imidazole nitrogen of the azoimine ligand should decrease the energy of transition, causing a red shift in

Table 1
Analytical,[a] FT IR, ^{1}H NMR[b] and ^{13}C NMR of complexes [**1**–**12**][PF_6]

Complex	Analyses (%)			IR (KBr pellets (cm^{-1}))	^{1}H NMR δ [multiplicity, nH, J (Hz)]	^{13}C NMR (δ)
	C	H	N			
1	38.6 (38.5)	3.9 (3.9)	9.4 (9.3)	3204 (ν_{N-H}), 1639 ($\nu_{C=N}$), 1434 ($\nu_{N=N}$), 844 (ν_{P-F})	1.38 (s, 15H, C_5Me_5), 6.97 (d, 2H, $^{3}J = 7.5$ Hz, Ph), 7.32–7.53 (m, 3H, Ph), 7.69 (d, 1H, $^{3}J = 6.4$ Hz, CH), 8.24 (d, 1H, CH), 9.21 (s, 1H, NH)	8.96, 96.47, 122.41, 124.36, 127.32, 129.49, 131.16, 134.90, 151.18
2	39.7 (40.0)	4.2 (4.2)	9.3 (9.1)	1633 ($\nu_{C=N}$), 1427 ($\nu_{N=N}$), 850 (ν_{P-F})	1.47 (s, 15H, C_5Me_5), 3.24 (s, 3H, CH_3), 7.47 (d, 2H, $^{3}J = 6.4$ Hz, Ph), 7.52–7.77 (m, 3H, Ph), 8.02 (d, 1H, $^{3}J = 7.2$ Hz, CH), 8.46 (d, 1H, CH)	8.91, 40.13, 92.92, 122.13, 126.42, 127.47, 130.27, 135.56, 142.55, 156.17
3	40.8 (40.8)	4.4 (4.3)	9.1 (9.1)	1633 ($\nu_{C=N}$), 1434 ($\nu_{N=N}$), 844 (ν_{P-F})	1.32 (s, 15H, C_5Me_5), 1.46 (t, 3H, $^{3}J = 4.5$ Hz, CH_3), 4.42 (q, 2H, CH_2), 7.07 (d, 2H, $^{3}J = 6.2$ Hz, Ph), 7.15–7.32 (m, 3H, Ph), 7.47 (d, 1H, $^{3}J = 6.1$ Hz, CH), 7.84 (d, 1H, CH)	8.91, 16.14, 44.16, 98.14, 122.19, 125.32, 127.62, 128.72, 133.74, 139.92, 146.11
4	39.7 (39.9)	4.2 (4.3)	9.3 (9.2)	3423 (ν_{N-H}), 1600 ($\nu_{C=N}$), 1447 ($\nu_{N=N}$), 850 (ν_{P-F})	1.71 (s, 15H, C_5Me_5), 2.53 (s, 3H, CH_3), 6.79 (d, 2H, $^{3}J = 6.1$ Hz, Ph), 6.93 (d, 2H, Ph), 7.58 (d, 1H, $^{3}J = 6.8$ Hz, CH), 7.99 (d, 1H, CH), 8.16 (s, 1H, NH)	9.26, 15.79, 86.19, 124.68, 127.38, 130.92, 131.17, 133.12, 136.19, 142.36
5	40.8 (40.6)	4.4 (4.4)	9.1 (9.2)	1606 ($\nu_{C=N}$), 1447 ($\nu_{N=N}$), 844 (ν_{P-F})	1.39 (s, 15H, C_5Me_5), 2.14 (s, 3H, CH_3), 3.42 (s, 3H, CH_3), 7.18 (d, 2H, $^{3}J = 6.8$ Hz, Ph), 7.42 (d, 2H, Ph), 7.71 (d, 1H, $^{3}J = 4.4$ Hz, CH), 8.24 (d, 1H, CH)	8.90, 22.46, 42.34, 97.16, 126.32, 127.41, 130.67, 132.31, 136.31, 141.46, 152.56
6	41.8 (41.7)	4.6 (4.4)	8.9 (8.9)	1626 ($\nu_{C=N}$), 1434 ($\nu_{N=N}$), 849 (ν_{P-F})	1.48 (t, 3H, $^{3}J = 6.9$ Hz, CH_3), 1.53 (s, 15H, C_5Me_5), 2.45 (s, 3H, CH_3), 4.55 (q, 2H, CH_2), 7.52 (d, 2H, $^{3}J = 8.4$ Hz, Ph), 7.86 (d, 2H, Hz, Ph), 8.01 (d, 1H, CH), 8.26 (d, 1H, CH)	9.31, 16.09, 21.76, 43.93, 99.21 124.22, 129.11, 130.59, 131.03, 144.79, 150.30, 155.01
7	33.6 (33.5)	3.4 (3.4)	8.2 (8.5)	3151 (ν_{N-H}), 1619 ($\nu_{C=N}$), 1467 ($\nu_{N=N}$), 850 (ν_{P-F})	1.47 (s, 15H, C_5Me_5), 7.13 (d, 2H, $^{3}J = 8.2$ Hz, Ph), 7.22–7.49 (m, 3H, Ph), 7.82 (d, 1H, $^{3}J = 8.1$ Hz, CH), 8.47 (d, 1H, CH), 9.12 (s, 1H, NH)	8.90, 92.86, 123.74, 124.29, 129.93, 130.42, 130.53, 133.17, 152.99
8	34.6 (34.4)	4.2 (4.3)	8.1 (8.2)	1633 ($\nu_{C=N}$), 1434 ($\nu_{N=N}$), 844 (ν_{P-F})	1.53 (s, 15H, C_5Me_5), 3.36 (s, 3H, CH_3), 7.69 (d, 2H, $^{3}J = 6.9$ Hz, Ph), 7.78–7.82 (m, 3H, Ph), 7.98 (d, 1H, CH), 8.30 (d, 1H, CH)	8.92, 39.89, 93.20, 124.46, 129.67, 130.01, 133.63, 151.68, 152.96, 160.96
9	35.6 (35.4)	3.8 (3.9)	7.9 (8.0)	1626 ($\nu_{C=N}$), 1440 ($\nu_{N=N}$), 844 (ν_{P-F})	1.36 (s, 15H, C_5Me_5), 1.52 (t, 3H, $^{3}J = 6.1$ Hz, CH_3), 4.26 (q, 2H, CH_2), 7.13 (d, 2H, $^{3}J = 7.3$ Hz, Ph), 7.23–7.41 (m, 3H, Ph), 7.53 (d, 1H, $^{3}J = 7.14$ Hz, CH), 7.91 (d, 1H, CH)	8.92, 14.13, 42.46, 94.36, 124.61, 126.52, 127.37, 130.49, 135.18, 146.63, 155.23
10	34.6 (34.6)	4.2 (4.6)	8.1 (8.7)	2925 (ν_{N-H}), 1606 ($\nu_{C=N}$), 1394 ($\nu_{N=N}$), 850 (ν_{P-F})	1.50 (s, 15H, C_5Me_5), 2.46 (s, 3H, CH_3), 7.46 (d, 2H, $^{3}J = 8.4$ Hz, Ph), 7.71 (d, 2H, Ph), 7.89 (d, 1H, $^{3}J = 10.6$ Hz, CH), 8.71 (d, 1H, CH), 9.07 (s, 1H, NH)	8.93 21.63, 92.65, 124.38, 127.47, 130.17, 130.32, 143.95, 150.93, 162.19
11	35.6 (35.4)	3.8 (3.7)	7.9 (7.9)	1633 ($\nu_{C=N}$), 1434 ($\nu_{N=N}$), 844 (ν_{P-F})	1.41 (s, 15H, C_5Me_5), 2.06 (s, 3H, CH_3), 3.53 (s, 3H, CH_3), 7.09 (d, 2H, $^{3}J = 6.4$ Hz, Ph), 7.44 (d, 2H, Ph), 7.68 (d, 1H, $^{3}J = 6.1$ Hz, CH), 8.09 (d, 1H, CH)	8.97, 21.37, 44.08, 99.42, 122.28, 125.37, 128.14, 130.36, 133.18, 139.92, 148.74
12	36.6 (36.6)	4.0 (4.1)	7.8 (7.7)	1637 ($\nu_{C=N}$), 1434 ($\nu_{N=N}$), 844 (ν_{P-F})	1.38 (s, 15H, C_5Me_5), 1.43 (t, 3H, $^{3}J = 5.4$ Hz, CH_3), 2.26 (s, 3H, CH_3), 4.44 (q, 2H, CH_2), 7.31 (d, 2H, $^{3}J = 6.6$ Hz, Ph), 7.82 (d, 2H, Ph), 8.14 (d, 1H, $^{3}J = 5.6$ Hz, CH), 8.32 (d, 1H, CH)	9.18, 15.69, 22.43, 46.15, 97.43, 123.72, 125.36, 128.93, 130.83, 133.68, 142.39, 152.35

[a] Calculated values are in parentheses.
[b] In $CDCl_3$; s, singlet; d, doublet; m, multiplet; $J_{(H-H)}$ in Hz.

Table 2
UV–Visible absorption data in dichloromethane at 298 K

Sl. no.	Complexes	λ_{max} (nm)			
1	$[(\eta^5\text{-}C_5Me_5)RhCl(Phai\text{-}H)]PF_6$	415	326		
2	$[(\eta^5\text{-}C_5Me_5)RhCl(Phai\text{-}Me)]PF_6$	407	370	358	
3	$[(\eta^5\text{-}C_5Me_5)RhCl(Phai\text{-}Et)]PF_6$	410	391	364	335
4	$[(\eta^5\text{-}C_5Me_5)RhCl(Tai\text{-}H)]PF_6$	423	365	313	
5	$[(\eta^5\text{-}C_5Me_5)RhCl(Tai\text{-}Me)]PF_6$	665	406	364	311
6	$[(\eta^5\text{-}C_5Me_5)RhCl(Tai\text{-}Et)]PF_6$	408	395	312	
7	$[(\eta^5\text{-}C_5Me_5)IrCl(Phai\text{-}H)]PF_6$	414	388	321	
8	$[(\eta^5\text{-}C_5Me_5)IrCl(Phai\text{-}Me)]PF_6$	446	393	316	
9	$[(\eta^5\text{-}C_5Me_5)IrCl(Phai\text{-}Et)]PF_6$	452	375	309	
10	$[(\eta^5\text{-}C_5Me_5)IrCl(Tai\text{-}H)]PF_6$	436	397	317	
11	$[(\eta^5\text{-}C_5Me_5)IrCl(Tai\text{-}Me)]PF_6$	407	333	311	
12	$[(\eta^5\text{-}C_5Me_5)IrCl(Tai\text{-}Et)]PF_6$	407	333	311	

MLCT maxima [17], while an electron withdrawing group should increase the transition energy. The electronic spectra of pentamethylcyclopentadienyl rhodium azoimine complexes (**1**–**6**) with the formulations $[\eta^5\text{-}C_5Me_5RhCl(RaaiR')]^+$ displayed very weak bands at 408–423 nm, a medium absorption band at ~390 nm and a very strong absorption band at ~330 nm (Table 2). The band at 390 nm has been assigned to a MLCT transitions [t_{2g} {Rh(III) → π*(azoimine)}]. The λ_{max} value of this band is consistent with those of the azoimine ligand bound to the complexes of rhodium [18].

The free ligand itself shows intraligand charge-transfer transitions (n–π*, π–π*) of high intensity ($\varepsilon \sim 10^4$–$10^5\ M^{-1}\ cm^{-1}$) at <400 nm. The transitions at ~350 nm and below are thus not considered further. Other two transitions at longer wavelength region (410–460 nm and 370–390 nm) differ in their intensities. The first transition (410–460 nm) is of moderate intensity and has been assigned to the MLCT band dπ(Rh) → π*(azoimine) in the complexes [19] or else from the hybrid orbitals composed of dπ(Rh) and π(Cp*) to the π*(azoimine) orbitals of the ligand. The weak transition at ~650 nm may originate from a singlet–triplet transition, particularly that allowed by the strong spin–orbit coupling in rhodium [20].

Electronic spectra of iridium complexes (**7**–**12**) display bands in the region ~450 nm, ~380 nm and ~320 nm. The broad medium intensity bands centering around 450 nm are assigned to MLCT bands arising from drift of electron density from the filled Ir(III) → dπ(t_{2g}) orbitals to the low lying π* orbitals of the RaaiR′ ligand. The position of this band is consistent with those in other metal-azo complexes [21]. The band around 320 nm is assigned to an MLCT transition [Ir(III) → dπ* on the Cp* ring].

2.2. Molecular structure of complex $[(\eta^5\text{-}C_5Me_5)RhCl(Me\text{–}C_6H_4\text{–}N{=}N\text{–}C_3H_3N_2)]^+$ (**4**)

The complex **4**[PF_6] crystallizes in the monoclinic $P2_1/n$ space group. The ORTEP drawing of the molecule along with the atom-numbering scheme is shown in Fig. 1. The asymmetric unit consists of a rhodium atom displaying

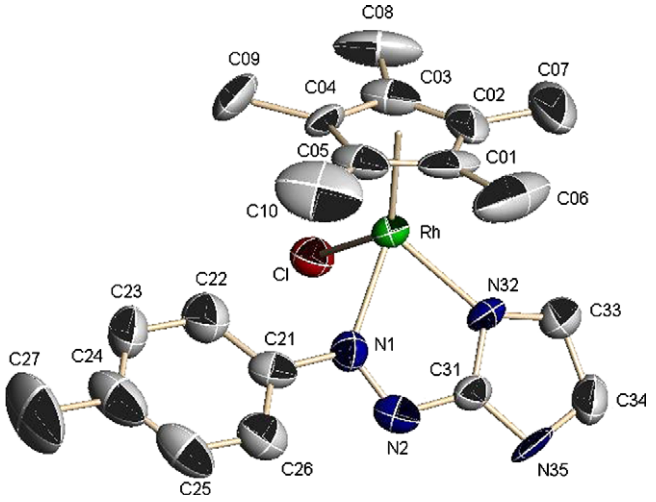


Fig. 1. ORTEP diagram of complex **4** at 50% probability level with hydrogen atoms and hexafluorophosphate anion omitted for clarity. Selected bond lengths (Å) and bond angles (°): Rh–N(1) 2.132(7), Rh–N(32) 2.105(8), Rh–Cl 2.423(3), N(1)–N(2) 1.275(10), Rh–C* 1.795 (* centroid is at $x = 0.7413$, $y = 0.1825$, $z = 0.9899$ at 1.795 Å to Rh); N(1)–Rh–N(32) 74.9(3), N(1)–Rh–Cl 92.5(2), N(32)–Rh–Cl 86.9(2).

the three-legged 'piano-stool' geometry. The metal is coordinated to one $\eta^5\text{-}C_5Me_5$ group, one chloride and two nitrogen atoms of Tai-H which binds to the metal in a bidentate chelating mode, as postulated from experimental data.

The pentamethylcyclopentadienyl ligand is symmetrically bound to the metal ion. All the Cp* atoms lie in a plane, and indicated by the similar bond distances between carbons. The Rh–Cl bond length is 2.432(3) Å which is slightly longer than the other two-coordinated chelating Schiff base rhodium complex $[(\eta^5\text{-}C_5Me_5)RhCl(C_5H_4N\text{-}2\text{-}CH{=}N\text{–}C_6H_4\text{-}p\text{-}Cl)]^+$ [2.3756(7) Å] [22].

The Rh–N distances are unequal with Rh–N(1), 2.132(7) Å and Rh–N(32), 2.105(8) Å. This has been observed in other complexes involving bidentate rhodium terpyridine $[(\eta^5\text{-}C_5Me_5)RhCl(Ph\text{-}terpy)]BF_4$ [23]. Rhodium to pentamethylcyclopentadienyl ring centroid distance is 1.759 Å and is consistent with those reported for the other rhodium(III) Cp* complexes [22]. The bond angles N(1)–Rh–Cl and N(32)–Rh–Cl are 92.5(2) and 86.9(2), respectively, indicating a piano stool type of structure at rhodium center. The N=N bond distance, N(1)–N(2) is 1.275(10) Å which is longer than free ligand value [1.250(1) Å] [24]. This refers to significant charge delocalization from metal d-orbital, dπ(Rh) → π*(azo) in the coordinated Tai-H.

3. Experimental

3.1. General remarks

$[\{(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl\}_2]$ (M = Rh, Ir) [25] and arylazoimidazole (RaaiR′) ligands [26] were prepared according to published methods. All other reagents were

commercially available and were used as received. UV/visible absorption spectra were recorded on a Hitachi – 300 spectrophotometer using precision cells made of quartz (1 cm). The ^{1}H and ^{13}C $\{^{1}H\}$NMR spectra were recorded in $CDCl_3$ solvent with TMS as internal standard and recorded on JEOL 500 (500 MHz) or Bruker ACF-300 (300 MHz) spectrometers, the coupling constants J are given in Hz. Infrared spectra were recorded as KBr pellets on a Perkin–Elmer-model-983 spectrophotometer. Microanalyses were performed on a Perkin–Elmer-2400 CHN/O analyzer, SAIF-NEHU, Shillong, India.

3.2. Synthesis of $[(\eta^5\text{-}C_5Me_5)RhCl(L)]PF_6$ {L = Phai-H (1), Phai-Me (2), Phai-Et (3), Tai-H (4), Tai-Me (5), Tai-Et (6)}

A mixture of $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ (100 mg, 0.16 mmol), arylazoimidazole (RaaiR′) (0.36 mmol) and potassium hexafluorophosphate (0.41 mmol) was stirred in dry methanol (20 mL) at 0 °C for 3 h. The solution becomes clear before the product precipitates. After 3 h the orange solid precipitated and the product was filtered, washed with diethylether (3 × 10 ml) and then dried *in vacuo* to afford 70–80% yield of the complexes.

3.3. Synthesis of $[(\eta^5\text{-}C_5Me_5)IrCl(L)]PF_6$ {L = Phai-H (7), Phai-Me (8), Phai-Et (9), Tai-H (10), Tai-Me (11), Tai-Et (12)}

These compounds was prepared by the same procedure as described above for [**1**–**6**][PF_6] using $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}Cl)(Cl)]_2$ (100 mg, 0.125 mmol), arylazoimidazole (RaaiR′) (0.26 mmol) and potassium hexafluorophosphate (0.41 mmol). Brown solid, Yield 65–75%.

4. Structure analysis and refinement

X-ray quality crystals of the complex **4**[PF_6] were grown by slow diffusion of hexane into dichloromethane solution. An orange crystal of complex **4**[PF_6] was mounted on a Bruker Apex CCD diffractometer in a full reciprocal sphere equipped with CCD detector and used for data collection. X-ray intensity data were collected with graphite monochromated Mo Kα radiation (0.71073 Å) at 293(2) K, with 0.3° scans in ω scan in mode and 10 s per frame. The intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction was made by modeling a transmission surface by spherical harmonics employing equivalent reflections with $I > 2\sigma(I)$ (program SADABS) [27]. The structure was solved by direct methods [28]. All the non-hydrogen atoms were refined anisotropically using the full-matrix, least-squares technique on F^2 using the SHELXL-97 software [29]. All the hydrogen atoms were found from difference Fourier synthesis after four cycles of anisotropic refinement using a ''riding'' model. A summary of crystal data, data collection parameters and convergence results is compiled in Table 3.

Table 3
Crystal data and structure refinement for complex **4**[PF_6]

Empirical formula	$C_{20}H_{25}ClF_6N_4PRh$
Formula weight	604.77
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P21/n$
Unit cell dimensions	
a (Å)	8.386(9)
b (Å)	27.72(3)
c (Å)	10.717(12)
β (°)	91.11(2)
Volume (Å^3)	2491(5)
Z	4
D_{calc} (Mg/m^3)	1.613
Absorption coefficient (mm^{-1})	0.917
$F(000)$	1216
Crystal size (mm)	0.15 × 0.10 × 0.07
θ Range for data collection (°)	1.47–28.26
Index ranges	$-9 \leqslant h \leqslant 9$, $-35 \leqslant k \leqslant 17$ $-13 \leqslant l \leqslant 4$
Reflections collected	7814
Independent reflections [R_{int}]	4514 [0.0796]
Completeness to theta (°, %)	28.26, 73.2
Absorption correction	Empirical
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4514/0/284
Goodness-of-fit on F^2	0.999
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0791$, $wR_2 = 0.1360$
R indices (all data)	$R_1 = 0.1839$, $wR_2 = 0.1696$
Largest difference peak and hole (e Å^{-3})	0.657 and −0.513

Appendix A. Supplementary material

CCDC 272064 contains the supplementary crystallographic data for **4**[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.2007.07.007.

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