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Pentamethylcyclopentadienyl ruthenium(II) complexes of *para*-substituted *N*-(pyrid-2-ylmethylene)-phenylamine ligands: syntheses, spectral and structural studies

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Abstract

The reaction of $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ (**1**) with acetonitrile in the presence of excess NH_4PF_6 leads to the formation of the cationic ruthenium(II) complex $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2(CH_3CN)]PF_6$ (**2**). The complex (**2**) reacts with a series of *N*,*N*′ donor Schiff base ligands viz. *para*-substituted *N*-(pyrid-2-ylmethylene)-phenylamines (ppa) in methanol to yield pentamethylcylopentadienyl ruthenium(II) Schiff base complexes of the formulation $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}X)]PF_6$ **[3a]PF$_6$**–**[3f]PF$_6$**, where C_5Me_5 = pentamethylcylopentadienyl, X = H, **[3a]PF$_6$**, Me, **[3b]PF$_6$**, OMe, **[3c]PF$_6$**, NO_2, **[3d]PF$_6$**, Cl, **[3e]PF$_6$**, COOH, **[3f]PF$_6$**. The complexes were isolated as their hexafluorophosphate salts. The complexes were fully characterized on the basis of elemental analyses and NMR spectroscopy. The molecular structure of a representative complex, $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}Cl)]PF_6$ **[3e]PF$_6$**, has been established by X-ray crystallography.

Keywords: Ruthenium; Pentamethylcyclopentadienyl; *N*-(pyrid-2-ylmethylene)-phenyl-amines; Pyridine-2-carboxaldehyde

1. Introduction

Half sandwich ruthenium(II) complexes have received great attention in the past few decades owing to their high reactivity ([1] and reference cited in) and catalytic activity [2]. The syntheses, structures and reactivity of half sandwich ruthenium(II) complexes viz., cyclopentadienyl, indenyl and arene have been studied in our laboratory. Our current interest has involved substitution of one triphenylphosphine and a chloride ligand of the complex $[Cp'Ru(PPh_3)_2Cl]$, where Cp′ = ind., Cp*, Cp with N-donor ligands [3,4], which is one of the key routes to explore their chemistry. There exist an extensive study on the chemistry of cyclopentadienyl ruthenium(II) with a variety of ligands [5]. In contrast, the analogous pentamethylcyclopentadienyl ruthenium(II) complexes have not been much studied. The chemistry of the pentamethylcylopentadienyl ruthenium fragment is largely based on the tetramer $[Cp^*RuCl]_4$ [6] and on the tris-acetonitrile $[Cp^*Ru(CH_3CN)_3]PF_6$ adduct [7], which upon addition of monodentate ligands yield octahedral complexes $[Cp^*RuX(L)_2]$ [8,9] and $[Cp^*Ru(L)_2(CH_3CN)]PF_6$ [7], respectively. However, to the best of our knowledge, pentamethylcylopentadienyl ruthenium(II) phosphine complexes chelated with *N*,*N*′ donor Schiff base ligands are not known, although there is an extensive chemistry available on arene and cyclopentadienyl ruthenium(II) [3b,10–12] systems.

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This present work arises from our interest to synthesize various half sandwich ruthenium(II) complexes containing N,N' donor Schiff base ligands. Having this in mind, we have previously described the syntheses of indenyl, cyclopentadienyl and arene [3,10] ruthenium(II) Schiff base complexes. In a continuation of our study, herein we report the syntheses of a series of pentamethylcyclopentadienyl ruthenium(II) Schiff base complexes **[3a]**PF_6–**[3f]**PF_6. The elemental analyses, spectral and structural characterization of the complexes is presented.

2. Experimental

2.1. General remarks

Reactions were carried out in distilled and dried solvents under nitrogen atmosphere. The solvents were purified according to the standard procedures. $RuCl_3\cdot 3H_2O$ was purchased from Arora Matthey (P) Ltd. and used as such. Pyridine-2-carboxaldehyde (Fluka) was used as received. All liquid aromatic amines were reagent grade and were distilled prior to use while solid aromatic amines were used as such. Microanalyses (C, H, N) were done by Regional Sophisticated Instrumentation Centre (RSIC), NEHU using a Perkin–Elmer-2400 CHNS/O analyzer. FT-IR spectra were recorded on a Perkin–Elmer-model 983 spectrophotometer with samples prepared as KBr pellets. Electronic spectra were recorded on a Hitachi-U-2300 spectrophotometer and conductivity measurements were done by Wayne Kerr Automatic Precession Bridge B905 using ca. 10^{-4} M solutions in dry acetonitrile at room temperature (Λ_m value in $S\,cm^2\,mol^{-1}$). The NMR spectra were obtained in $CDCl_3$ solution and recorded on a Bruker ACF-300 MHz spectrometer. Chemical shifts are relative to TMS (^1H, $^{13}C\{^1H\}$) and to 85% H_3PO_4 ($^{31}P\{^1H\}$); coupling constants are given in hertz. The ligands (C_5H_4N-2-CH=N-C_6H_4-*p*-X), (where X = H, Me, OMe, Cl, NO_2, COOH) [13] were prepared by the condensation of pyridine-2-carboxaldehyde with the appropriate amines. The precursor complex [(η^5-C_5Me_5)Ru(PPh_3)$_2$Cl] [14] was prepared by following the literature method.

2.2. Preparation of [(C_5Me_5)Ru(PPh_3)$_2$($NCCH_3$)]PF_6 [2]PF_6

The complex was prepared by following the literature method [15] as delineated here. The complex [Cp*Ru(PPh_3)$_2$Cl] (0.1 g, 0.125 mmol) and NH_4PF_6 (0.041 g, 0.250 mmol) were refluxed in CH_3CN (30 ml) for 2 h. During this time the orange red suspension turned yellow and a white solid appeared. The white solid was filtered off and the filtrate was rotary evaporated. The yellow residue was dissolved in dichloromethane (5 ml) and filtered to remove excess NH_4PF_6. The filtrate on concentration and addition of excess hexane gave a yellow crystalline solid. The yellow solid was collected and washed with hexane to afford 83% yield of complex (**2**).

^1H NMR ($CDCl_3$, δ): 1.32 (s, 15H, Cp), 2.17 (s, 3H, CH_3CN), 6.78–7.83 (m, 30H).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 45.28 (s. 2P, PPh_3), −143 (septet, PF_6^-).

2.3. Preparation of [(η^5-C_5Me_5)Ru(PPh_3)(C_5H_4N-2-CH=N-C_6H_4-p-X)]PF_6 [X = H [3a]PF_6, Me [3b]PF_6, OMe [3c]PF_6, NO_2 [3d]PF_6, Cl [3e]PF_6, COOH [3f]PF_6

These complexes were prepared by using a general method.

The complex (**2**), (0.1 g, 0.105 mmol) and the appropriate ligand (0.210 mmol) were mixed in 20 ml of methanol. After a few minutes the yellow solution turned into a dark brown suspension. The mixture was refluxed for 1 h under nitrogen atmosphere. The solution was cooled to room temperature and solvent was removed in a rotary-evaporator to dryness. The brown residue was dissolved in dichloromethane (5 ml) and filtered through a short silica gel column. The filtrate on subsequent concentration and addition of excess diethyl ether gave complexes **[3a]**PF_6–**[3f]**PF_6 as dark brown solids in 81–87% yield.

2.4. Analytical and spectroscopic data

2.4.1. [(η^5- C_5Me_5)Ru(PPh_3)(C_5H_4N-2-CH=N-C_6H_5)]-PF_6 [3a]PF_6

Yield: 83% (72 mg). *Anal.* Calc. for $C_{40}H_{40}N_2P_2F_6Ru$: C, 58.13; H, 4.81; N, 3.39. Found: C, 57.6; H, 5.01; N, 3.45%. IR (KBr, cm^{-1}): $\nu_{(C=N)}$ 1600, $\nu_{(PF_6^-)}$ 844.

^1H NMR ($CDCl_3$, *J* Hz): δ 1.31 (s, 15H, C_5Me_5); 7.14 (d, 2H, J_{H-H} = 2.89); 7.18–7.64 (m, 21H); 8.25 (d, 1H, 2.64); 8.92 (d, 1H, 3.38).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.31 (s, $C_5Me_5(CH_3)$); 88.73 (s, C_5Me_5 (ring)); 122.46–151.26 (phenyl and pyridyl carbons); 157.83 (N=CH).

$^{31}P\{^1H\}$ NMR: δ 45.26 (s, PPh_3); −141 (septet, PF_6^-).

2.4.2. [(η^5-C_5Me_5)Ru(PPh_3)(C_5H_4N-2-CH=N-C_6H_4-p-Me)]PF_6 [3b]PF_6

Yield: 86% (76 mg). *Anal.* Calc. for $C_{41}H_{42}N_2P_2F_6Ru$: C, 58.59; H, 5.00; N, 3.33. Found: C, 59.35; H, 4.99; N, 3.67%.

IR (KBr, cm^{-1}): $\nu_{(C=N)}$ 1598, $\nu_{(PF_6^-)}$ 844.

^{1}H NMR ($CDCl_3$, J Hz): δ 1.31 (s, 15H, C_5Me_5); 2.38 (s, 3H); 7.07 (d, 2H, J_{H-H} = 5.73); 7.18 (d, 2H, J_{H-H} = 4.82); 7.29–7.62 (m, 18H); 8.22 (d, 1H, J_{H-H} = 3.48); 8.92 (d, 1H, J_{H-H} = 3.38).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.23 (s, $C_5Me_5(CH_3)$); 15.29 (s, Me); 88.47 (s, C_5Me_5 (ring)); 123.48–152.01 (phenyl and pyridyl carbons); 160.46 (N=CH).

$^{31}P\{^1H\}$ NMR: δ 46.55 (s, PPh_3); −142 (septet, PF_6^-).

2.4.3. *[(η^5-C_5Me_5)Ru(PPh_3)(C_5H_4N-2-CH=N-C_6H_4-p-OMe)]PF_6 [3c]PF_6*

Yield: 87% (78 mg). *Anal.* Calc. for $C_{41}H_{42}N_2OP_2F_6Ru$: C, 57.49; H, 4.91; N, 3.27. Found: C, 56.29; H, 4.97; N, 3.54%.

IR (KBr, cm^{-1}): $\nu_{(C=N)}$ 1602, $\nu_{(PF_6^-)}$ 844.

^{1}H NMR ($CDCl_3$, J Hz): δ 1.32 (s, 15H, C_5Me_5); 3.84 (s, 3H); 6.77 (d, 2H, J_{H-H} = 5.73); 7.13–7.65 (m, 20H); 8.24 (d, 1H, J_{H-H} = 2.97); 8.87 (d, 1H, J_{H-H} = 5.10).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.24 (s, $C_5Me_5(CH_3)$); 88.42 (s, C_5Me_5 (ring)); 113.99 (s, OCH_3); 125.48–151.88 (phenyl and pyridyl carbons); 161.66 (N=CH).

$^{31}P\{^1H\}$ NMR: δ 46.63 (s, PPh_3); −143 (septet, PF_6^-).

2.4.4. *[(η^5- C_5Me_5)Ru(PPh_3)(C_5H_4N-2-CH=N-C_6H_4-p-NO_2)]PF_6 [3d]PF_6*

Yield: 81% (74 mg). *Anal.* Calc. for $C_{40}H_{39}N_3O_2P_2F_6Ru$: C, 55.12; H, 4.47; N, 4.82. Found: C, 55.96; H, 4.73; N, 4.26%.

IR (KBr, cm^{-1}): $\nu_{(C=N)}$ 1608, $\nu_{PF_6^-}$ 844.

^{1}H NMR ($CDCl_3$; J Hz): δ 1.32 (d, 15H, C_5Me_5 J_{P-H} = 1.09); 6.93 (d, 2H, J_{H-H} = 2.89); 7.18–7.96 (m, 18H); 8.15 (d, 2H, J_{H-H} = 6.12); 8.41 (d, 1H, J_{H-H} = 3.34); 8.93 (d, 1H, 3.59).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.45 (s, $C_5Me_5(CH_3)$); 88.91 (s, C_5Me_5 (ring)); 124.86–151.99 (phenyl and pyridyl carbons); 162.38 (N=CH).

$^{31}P\{^1H\}$ NMR: δ 47.23 (s, PPh_3); −141 (septet, PF_6^-).

2.4.5. *[(η^5- C_5Me_5)Ru(PPh_3)(C_5H_4N-2-CH=N-C_6H_4-p-Cl)]PF_6 [3e]PF_6*

Yield: 87% (76 mg). *Anal.* Calc. for $C_{40}H_{39}N_2P_2F_6ClRu$: C, 55.84; H, 4.53; N, 3.25. Found: C, 54.20; H, 4.73; N, 3.12%.

IR (KBr, cm^{-1}): $\nu_{(C=N)}$ 1612, $\nu_{(PF_6^-)}$ 844.

^{1}H NMR ($CDCl_3$, J Hz): δ 1.32 (s, 15H, C_5Me_5); 6.83 (d, 2H, J_{H-H} = 3.24); 6.94–7.67 (m, 20H); 8.29 (d, 1H, J_{H-H} = 1.98); 8.90 (d, 1H, J_{H-H} = 4.73).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.45 (s, C_5Me_5); 88.73 (s, C_5Me_5 (ring)); 125.19–152.07 (phenyl and pyridyl carbons); 161.83 (N=CH).

$^{31}P\{^1H\}$ NMR: δ 46.53 (s, PPh_3); −143 (septet, PF_6^-).

2.4.6. *[(η^5- C_5Me_5)Ru(PPh_3)(C_5H_4N-2-CH=N-C_6H_4-p-CO_2H)]PF_6 [3f]PF_6*

Yield: 84% (77 mg). *Anal.* Calc. for $C_{41}H_{40}N_2O_2P_2F_6Ru$: C, 55.22; H, 4.60; N, 3.22. Found: C, 54.75; H, 4.83; N, 3.46%.

IR (KBr, cm^{-1}): $\nu_{(C=N)}$ 1610, $\nu_{(PF_6^-)}$ 844.

^{1}H NMR ($CDCl_3$, J Hz): δ 1.31 (s, 15H, C_5Me_5); 6.64 (d, 2H, J_{H-H} = 6.73); 7.37–8.05 (m, 17H); 8.02 (d, 2H, J_{H-H} = 4.02); 8.34 (d, 1H, J_{H-H} = 2.63); 8.62 (s, 1H); 8.95 (d, 1H, J_{H-H} = 5.22).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.42 (s, C_5Me_5 (CH_3)); 88.86 (s, C_5Me_5 (ring)); 124.05–155.96 (phenyl and pyridyl carbons); 160.46 (N=CH), 178.26 (C(CO_2H)).

$^{31}P\{^1H\}$ NMR: δ 47.28 (s, PPh_3); −145 (septet, PF_6^-).

2.5. Structure analysis and refinement

X-ray quality crystals of complex **[3e]PF_6** were grown by slow diffusion of hexane into a dichloromethane solution of complex **[3e]PF_6**. The X-ray intensity data were collected on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at 143 K. Intensity data were corrected for Lorentz and polarization effects and for absorption correction using REQAB [16]. The structure was solved by direct methods (SIR 97) [17] and refinement was by full matrix least squares based on F^2 using (SHELXL-97) [18]. The weighting scheme used was $W = 1/[\sigma^2(F_0^2) + 0.0822P^2 + 3.3880P]$, where $P = (F_0^2 + 2F_c^2)/3$. The X-ray data were corrected for the presence of disordered solvent using "SQUEEZE" [19]. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a "riding" model.

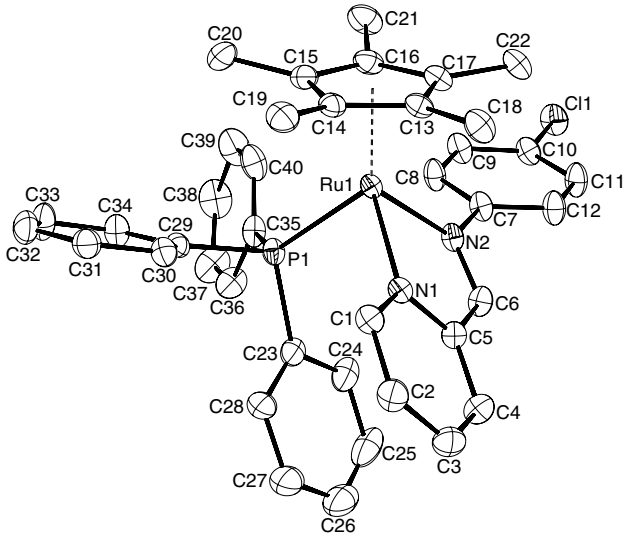


Fig. 1. Molecular structure of complex **[3e]PF_6** with 30% thermal ellipsoids. Hydrogen atoms and the PF_6 ion have been omitted for clarity.

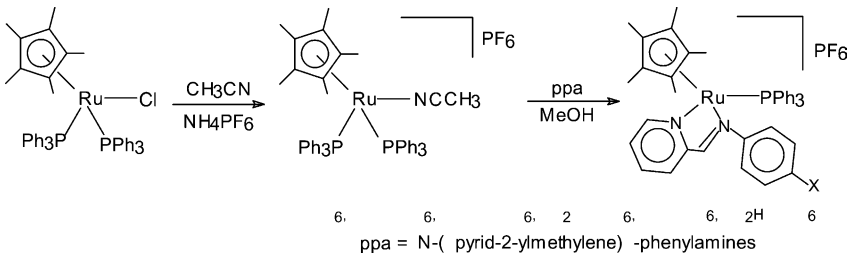
Refinement converged to $R_1 = 0.0444$ and $wR_2 = 0.1267$. Fig. 1 is an ORTEP [20] representation of the molecule with 30% thermal ellipsoids displayed.

3. Results and discussion

While N-chelating cyclopentadienyl ruthenium(II) complexes are well known [3b,5,10], only a few reports about the analogous pentamethylcyclopentadienyl are available in the literature [4]. Here we described the preparation of six new monocationic pentamethylcyclopentadienyl ruthenium(II) phosphine complexes **[3a]PF$_6$**–**[3f]PF$_6$** containing *N*,*N*′ donor Schiff base ligands, and their characterization with the help of elemental analyses, IR and NMR (^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H}) spectroscopy. The molecular structure of a representative complex **[3e]PF$_6$** was determined by a single X-ray study. To the best of our knowledge this complex is the first structurally characterized pentamethyl-cyclopentadienyl ruthenium(II) Schiff base complex containing a phosphine ligand. The complexes were obtained in good yield, by reacting complex **[2]PF$_6$** with the appropriate ligands in methanol as depicted in Scheme 1.

We have recently synthesized cyclopentadienyl ruthenium(II) complexes of Schiff base ligands such as $[CpRu(PPh_3)(ppa)]^+$ [3b] by reacting the ligand (ppa) with the complex $[CpRu(PPh_3)_2Cl]$. However, in this present case the complexes are readily obtained in high yields by the reaction of the acetonitrile complex **[2]PF$_6$** with the appropriate ligand. These complexes can also be prepared in lower yield by the reaction of complex (**1**) with the ligand over a longer period of time. This suggests the acetonitrile complex **[2]PF$_6$** is a better precursor than their chloro analog (**1**) for the preparation of these complexes **[3a]PF$_6$**–**[3f]PF$_6$**. This is due to the cationic nature of the complex **[2]PF$_6$** which makes ready coordination of the ligand to the metal atom compared to the neutral chloro complex (**1**). It has been reported that the pentamethylcyclopentadienyl complexes, $[Cp^*Ru(PPh_3)_2Cl]$ are much more reactive than the analogous cyclopentadienyl complexes, which is attributed to the electron rich nature of the Cp* ligand and the presence of five sterically hindered methyl groups associated with these complexes which facilitates ready dissociation of one of the triphenylphosphine ligands. In fact, one triphenylphosphine can be readily substituted by diazonium salts from $[Cp^*Ru(PPh_3)_2Cl]$ irrespective of the solvent used (acetone or toluene), in contrast the same substitution is only possible in the analogous $[CpRu(PPh_3)_2Cl]$ complex using toluene under drastic conditions [21]. It is notable that the Cp* ligand is less stable as compared to the analogous Cp ligand and that prolonged reaction under drastic conditions results in removal of the Cp* ligand from the complex. Very recently we have studied the reaction of $[Cp'Ru(PPh_3)_2Cl]$, [where Cp′ = ind., Cp*, Cp] with sterically demanding the multidentate tetra-2-pyridyl-1,4-pyrazine (tppz) ligand, where attempts to synthesis Cp* and indenyl complexes chelated with the tppz ligand were unsuccessful, instead we isolated complexes of the type $[(tppz)Ru(PPh_3)_2X]$ [22]. However, when the reaction was carried out with $[CpRu(PPh_3)_2Cl]$, the η^5-bonded cyclopentadienyl group remained intact to the metal thus forming a complex of the type $[CpRu(L_2)(PPh_3)]^+$ [5b]. This indicates the more labile nature of the indenyl and Cp* ligands as compared to the cyclopentadienyl ligand.

The complexes **[3a]PF$_6$**–**[3f]PF$_6$** are highly soluble in polar solvents but insoluble in non-polar solvents. The conductivity measurement (10^{-4} in CH_3CN) of the complexes showed the complexes are ionically dissociated into a 1:1 electrolytic system [23]. The microanalyses data of the complexes are in good agreement with that of their formulations. The IR spectra of the complexes exhibit bands corresponding to $\nu_{C=N}$ of the coordinated ligands at 1598–1612 cm^{-1}, while ν_{P-F} of the PF_6^- counter ion appears at 844 cm^{-1}. The IR spectra showed a shift of the C=N stretching frequency towards lower wavenumbers as compared with the free base ligands (1598–1612 versus 1619–1638 cm^{-1}) indicating N-coordination of the C=N group [24]. The complex (**[3d]PF$_6$**) showed a characteristic IR band for symmetric ν_{NO_2} and asymmetric ν_{NO_2} at 1348 and 1458 cm^{-1}, respectively, similar to those observed for other reported compounds. The proton NMR spectra of these complexes displayed a sharp singlet (except **[3d]PF$_6$**) at δ 1.3 for the methyl protons of the pentamethylcyclopentadienyl while for the complex **[3d]PF$_6$** the resonance is observed as a doublet.



Scheme 1. X = H, **[3a]PF$_6$**; Me, **[3b]PF$_6$**; OMe, **[3c]PF$_6$**; NO_2, **[3d]PF$_6$**; Cl, **[3e]PF$_6$**; COOH, **[3f]PF$_6$**.

The doublet observed could be due to the coupling of methyl protons of the Cp* moiety with the phosphorus of the triphenylphosphine. The resonance of ortho proton of the pyridine ring of the ligand appeared as a doublet in the range of δ 8.87–8.95. The doublet observed was probably due to coupling of the methine proton with the proton of the aromatic ring of the coordinated ligands. However, this proton appears as singlet at δ 8.6 in the case of the complex **[3f]PF$_6$**. We did not observe the resonance for the acidic proton CO_2H in the proton NMR spectrum of the complex **[3f]PF$_6$**. The spectra of all these complexes also contained multiple resonances for the aromatic protons in the range of δ 6.94–8.05. The $^{13}C\{^1H\}$ NMR spectra of the complexes contained resonances for C_5Me_5 carbons at around δ 9.49 for the methyl group of Cp* and δ 89.26 for the ring carbons. The resonance observed at around δ 161 could be due to the imine carbon (CH=N) of the Schiff base ligand. The $^{13}C\{^1H\}$ NMR spectrum of complex **[3f]PF$_6$** showed a singlet at δ 178, which is assignable to the carbon of COOH. The spectra also showed resonances in the range of δ 123.48–155.96 for the aromatic carbons and carbons of the pyridyl ring. The $^{31}P\{^1H\}$ NMR spectra of the complexes displayed a singlet in the range of δ 45.26–46.7 due to the triphenylphosphine moiety as compared to δ 38.5, observed in the neutral precursor complex $[Cp^*Ru(PPh_3)_2Cl]$. The spectra also contained a septet in the range of δ −141 to −145 for the PF_6^- counter ion. The electronic spectra of the complexes in dichloromethane exhibited absorption bands in the range of 475–493 nm (Table 1). These low energy absorption bands present in all of these complexes are characteristics of Ru(dπ)–L(π^*), metal to ligand charge transfer transitions (MLCT).

3.1. Crystal structure

The crystal structure determination was carried out for the representative complex **[3e]PF$_6$**. There is a disordered area in the crystal, which was a combination of PF_6's and dichloromethane, the solvent of crystallization. The space group has four symmetry-related positions in the unit cell, of which the PF_6's ions occupy two and the other two by the CH_2Cl_2 molecules. The effect of this disorder was removed from the data using the "SQUEEZE" program, which was written to correct data for the presence of disordered solvents [19]. The perspective view of the cationic part of the complex with the numbering scheme of the atoms is shown in Fig. 1. Details of the crystallographic data collection are given in Table 2. Selected bond lengths and angles are presented in Table 3.

The complex crystallized in the $P2_1/c$ space group and consists of complex cation and PF_6 anions joined by columbic forces. The ruthenium atom presents a pseudo-octahedral environment with the Cp* ligand occupying three facile coordination sites, π-bonded to the metal in η^5-fashion, while the remaining coordination positions are occupied by the P atom of the triphenylphosphine

Table 2
Summary of structure determination of complex **[3e]PF$_6$**

Formula	$C_{40}H_{39}N_2P_2F_6ClRu$
Formula weight	860.19
Crystal class	monoclinic
Space group	$P2_1/c$ (#14)
Z	4
Cell constants	
a (Å)	10.7236(5)
b (Å)	19.9676(9)
c (Å)	18.6390(9)
β (°)	98.3575(4)
V (Å^3)	3948.7(3)
μ (cm^{-1})	6.05
Crystal size (mm)	$0.40 \times 0.35 \times 0.30$
D_c (g/cm^3)	1.447
$F(000)$	1752
Radiation	Mo Kα (λ = 0.71069 Å)
2θ range	5.12–54.96
hkl collected	$-13 \leqslant h \leqslant 13$; $-25 \leqslant k \leqslant 23$; $-23 \leqslant l \leqslant 24$
Number of reflections measured	24 099
Number of unique reflections	8816 (R_{int} = 0.0191)
Number of observed reflections	7696 ($F > 4\sigma$)
Number of reflections used in refinement	8816
Number of parameters	445
R indices ($F > 4\sigma$)	R_1 = 0.0444; wR_2 = 0.1267
R indices (all data)	R_1 = 0.0499; wR_2 = 0.1332
GOF	1.052
Final difference peaks (e/Å^3)	+1.566, −0.656

Table 1
UV–Vis and conductivity data of the complexes at room temperature

No.	Complexes	λ_{max} (nm)	Conductivity Λ_m (S cm^2 mol^{-1})
1.	$[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_5)]PF_6$ **[3a]PF$_6$**	486	180
2.	$[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}CH_3)]PF_6$ **[3b]PF$_6$**	490	172
3.	$[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}OMe)]PF_6$ **[3c]PF$_6$**	475	159
4.	$[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}NO_2)]PF_6$ **[3d]PF$_6$**	482	167
5.	$[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}Cl)]PF_6$ **[3e]PF$_6$**	493	145
6.	$[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(C_5H_4N\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}p\text{-}CO_2H)]PF_6$ **[3f]PF$_6$**	478	169

Table 3
Molecular structure of complex [**3e**]PF_6 with 30% thermal ellipsoids

Bond lengths (Å)			
Ru–N(1)	2.106(2)	Ru–P(1)	2.3593(7)
Ru–N(2)	2.097(2)	N(2)–C(6)	1.297(4)
C*–Ru	1.8536(2)		
C* = centroid of C(13), C(14), C(15), C(16), C(17)			
Bond angles (°)			
N(1)–Ru–N(2)	75.67(9)	N(1)–Ru–P(1)	88.79(6)
N(2)–Ru–P(1)	92.84(6)		

Hydrogen atoms and the PF_6 ion have been omitted for clarity.

and N atoms of the Schiff base ligand. The average bond distance of ruthenium to ring carbon is 2.2198 Å, whereas the distance between the ruthenium and the centroid of the ring is 1.8536(2) Å. The Ru–P(1) bond length, 2.3593(7) Å, is within the usual range of Ru–P bond distances (2.20–2.43 Å) [25]. The ruthenium and nitrogen bond distances, 2.106(2) and 2.097(2) Å, are within the range of reported compounds. There is no significant difference in the C–C bond lengths in the cyclopentadienyl ring. The bond lengths falls within the range of 1.418(4)–1.452(4) Å, suggesting the delocalization of π-electrons in the ring. Further, the five-membered ring is planar as evident by the nearly equal bond distances between the ruthenium and ring carbons. The angle between N(1)–Ru(1)–N(2), 75.67(9)°, is very close to those reported for the similar ligand in indenyl ruthenium(II) complexes [3a]. The complex adopts the familiar ''piano stool'' structure as evident by the nearly 90° bond angles for N(1)–Ru–P(1) (88.79(6)°) and N(2)–Ru–P(1) (92.84(6)°).

4. Conclusions

The present study describes the simple synthetic methodology for the preparation of six new monocationic pentamethylcyclopentadienyl ruthenium(II) Schiff base complexes. Complex [**3e**]PF_6 provides a first insight into the structural data of pentamethylcyclopentadienyl ruthenium(II) Schiff base complexes containing a phosphine ligand.

Appendix A. Supplementary data

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre (CCDC), CCDC No. 252029 for complex **3e**. Copies of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.poly.2004.11.021.

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