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New mononuclear ruthenium complexes of η^5-cyclichydrocarbon containing azine ligands: Syntheses, spectral and structural studies

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Abstract

A series of mononuclear indenyl and pentamethylcyclopentadienyl ruthenium(II) complexes of formulation $[(\eta^5\text{-}L_3)Ru(PPh_3)(L_2)]X$, (where L_3 = indenyl, pentamethylcyclopentadienyl; X = PF_6 or BF_4 and L_2 = azine ligands) have been prepared by the reaction of $[(\eta^5\text{-}L_3)Ru(PPh_3)_2(CH_3CN)]X$ with the appropriate azine ligands in methanol or dichloromethane/benzene mixture. The reaction of nitro substituted azine ligands with the complexes $[(\eta^5\text{-}L_3)Ru(PPh_3)_2(CH_3CN)]X$ are solvent dependent. All these complexes were isolated as their PF_6 or BF_4 salts. The complexes were fully characterized with the help of microanalyses, FT-IR and NMR spectroscopy. The molecular structure of representative complexes **5c** and **6a** were established by single X-ray crystallography.

Keywords: Indenyl; Pentamethylcyclopentadienyl; Pyridine-2-carboxaldehyde; 2-acetylpyridine; Azine; Ruthenium

1. Introduction

Half sandwich complexes of platinum group metals have been proved to be extremely useful in stoicheometric and catalytic asymmetric syntheses and have therefore attracted much study [1–5]. Extensive studies on chemistry of half sandwich ruthenium complexes of cyclopentadienyl are known [6]. However the analogous indenyl and pentamethylcyclopentadienyl complexes have remained relatively unexplored. It is well known that η^5-indenyl complexes display enhanced reactivity in both S_N1 [7,8] and S_N2 [7–11] substitution reactions, compared with their cyclopentadienyl analogues. Recent kinetic studies [7,10], indicate the relative ease of slippage of the indenyl ring from η^5- to η^3-coordination during S_N2 substitution reaction at 18-electron metal centers. The relative ease of ring slippage for indenyl vs. cyclopentadienyl ligands has generally been attributed to the rehybridization of indenyl π-system, which involves an increase in the aromatic character of the benzene ring [7–10]. The chemistry of the complexes $[Cp'Ru(PPh_3)_2Cl]$ (where, Cp′ = indenyl, Cp or Cp*) are characterized by ready displacement of one triphenylphosphine or one triphenylphosphine along with chloride ion to yield neutral or cationic complexes [12]. Over the decades, syntheses of half sandwich complexes containing N-donor ligands such as polypyridyl, azo

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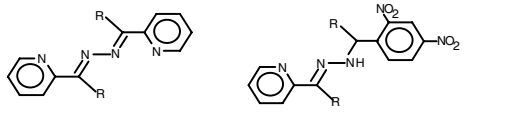
and Schiff's base have received considerable attention due to their interesting photophysical, photochemical properties and potential use in several fields viz., photochemical molecular devices, in solar energy conversion, as light sensitive probes in biological systems and as photosensitizers in redox reaction, and catalytic properties [13].

Literature survey reveals that most of the study on indenyl and pentamethylcyclopentadienyl ruthenium (II) complexes are centered on the reactivity study of these complexes towards alkenes and alkynes [14,15]. However, indenyl or Cp* phosphine complexes containing N-based ligands of the type $[Cp'Ru(PPh_3)(LL)]^+$ are virtually unknown except our group reported a few of such complexes in the recent years [16,17]. We have previously described the syntheses of indenyl (ind) [16a] and pentamethylcyclopentadienyl (Cp*) [16b] ruthenium (II) complexes of bidentate N,N′ donor Schiff's base ligands. However, our attempt to synthesize analogous complex of sterically demanding multidentate tetra-2-pyridyl-1,4-pyrazine (tppz) ligand were so far unsuccessful, instead we isolated complexes of the type $[(tppz)Ru(PPh_3)_2X]$ (where, X = CH_3CN, Cl) resulted from the displacement of indenyl or Cp* moiety by the tppz ligand [18]. This observation suggest that the stability of indenyl or Cp* ligands largely depend on the steric nature of the incoming ligand. In general, reactions with sterically demanding multidentate ligands displaced the organic fragment viz., Cp* and indenyl from the complex. It is well known that complexes of indenyl and Cp* are highly reactive which are attributed to the ring slippage from η^5- to η^3- and back to η^5- of the indenyl ligand in the case of indenyl complexes while electron rich nature of methyl group is the entirely responsible in the Cp* complexes [19]. The high reactivity of such complexes and labile nature of the indenyl or Cp* ligand poised practical difficulties on the syntheses of their complexes containing sterically multidentate N-base ligands.

To the best of our knowledge indenyl and pentamethylcyclopentadienyl ruthenium complexes of azine ligands have not been studied [20]. In continuation of our study on the reaction of indenyl and pentamethylcyclopentadienyl complexes with various N-base ligands herein, we described the syntheses of a series of indenyl and pentamethylcyclopentadienyl ruthenium (II) complexes with some azine ligands. The ligands involved in the study are shown in Scheme 1. The complexes were characterized with the help of ^1H and ^{31}P $\{^1H\}$ NMR spectroscopy. The structure of representative complexes **5c** and **6a** were established by single X-ray study.



R= H, Bis (2-Pyridyl) Ketazine (bpk)
R=Me,Bis (2-Pyridyl methyl) ketazine (bpmk)

R=H,2-Pyridyl-2,4-dinitro phenyl Ketazine (pdk)
R= Me, 2-Pyridylmethyl-2,4-dinitro phenyl Ketazine (pdmk)

Scheme 1.

2. Experimental

All synthetic operations were performed in a nitrogen atmosphere. Solvents were dried over appropriate drying agents, and then distilled prior to use [21]. The ligands were made by the condensation of pyridine-2-carboxaldehyde or 2-acetylpyridine with the appropriate hydrazine [22]. The starting materials, $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ (**1**) [23] and $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ (**2**) [15] were prepared following the literature methods while the complexes $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2(CH_3CN)]PF_6$ (**3**) [23] and $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2(CH_3CN)]BF_4$ (**4**) [24] were prepared by minor modifications of the literature procedures as described below. The NMR spectra were recorded on Bruker ACF-300 MHz and Bruker AMX-400 MHz instruments with $SiMe_4$ as an internal standard. Chemical shift for ^{31}P resonances were referred to 85% H_3PO_4. Infrared spectra were recorded as a KBr pellets on a Perkin–Elmer model 983 spectrometer. Electronic spectra were recorded on a Hitachi-U-2300 spectrophotometer in dichloromethane (ca. 10^{-4} M). Micro analytical data were obtained from Regional Sophisticated Instrumentation Centre (RSIC) NEHU, Shillong, using a Perkin–Elmer 2400 CHN/S analyzer.

2.1. Preparation of $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2(CH_3CN)]PF_6$ (3)

The complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ (**1**) (100 mg, 0.128 mmol) and NH_4PF_6 (39 mg, 0.24 mmol) were refluxed in 30 ml of acetonitrile for 2 h. During this time, the solution turned yellow and white solid was appeared. The solution was filtered to remove the white solid. The filtrate was rotary evaporated to dryness and the residue was dissolved in dichloromethane and filtered into 50 ml of hexane, whereby the product precipitated out as a yellow crystalline solid.

^1H NMR ($CDCl_3$, δ): 2.3(s, 3H), 4.5 (d, 2H, indenyl), 4.7 (t, 1H, indenyl), 6.9–7.8 (m, 34H). NMR (δ_P, $CDCl_3$): 54.55.

2.2. Preparation of $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2(CH_3CN)]BF_4$ (4)

The complex was prepared in analogy to (**3**) as described above using $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ (**2**) and NH_4BF_4 instead of $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ and NH_4PF_6.

^1H NMR ($CDCl_3$, δ): 1.32 (s, 15H, C_5Me_5), 2.17 (s, 3H, CH_3CN), 6.78–7.83 (m, 30 H). NMR (δ_P, $CDCl_3$): 45.28.

2.3. Preparation of new complexes

2.3.1. $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(bpk)]PF_6$ (**5a**)

The complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2(CH_3CN)]PF_6$(1) (100 mg, 0.107 mmol), the ligand bpk (50 mg, 0.22 mmol) and methanol (40 ml) were mixed in a round bottom flask. The mixture was refluxed for 3 h under nitrogen atmosphere, and the solution became dark brown as the reaction proceeded. The solution on evaporation to dryness by rotary evaporator afforded a brown residue, which was purified by column chromatography on silica gel using a dichloromethane-acetone (5:1, v/v) mixture as eluent. The solution on subsequent concentrated to ca. 5 ml and addition of excess hexane induce a dark brown solid. Yield: 70 mg, 78%.

NMR (δ_H,$CDCl_3$): 9.80 (d, 1H, ^3J(HH) = 5.14), 8.84 (d, 1H, ^3J(HH) = 4.55), 8.12 (s, 1H) 8.09 (s, 1H), 8.02 (dt, 1H, ^3J(HH) = 1.58, ^4J(HH) = 7.5), 7.87 (dt, 1H, unresolved), 6.69–7.33 (m, 23H), 5.26 (d, 2H, ^3J(HH) = 2.38, indenyl), 4.73 (t, 1H, ^3J(HH) = 2.53, indenyl). NMR (δ_P, $CDCl_3$): 55.84. IR (KBr, cm^{-1}): 1628, 1613 $\nu_{(C=N)}$, 844 $\nu_{(PF6)}$. UV–vis ($\lambda_{max,}$ nm): 456. Anal. Calc. for $C_{39}H_{32}N_4P_2F_6Ru$: C, 56.2; H, 3.8; N, 6.7. Found: C, 55.8; H, 3.6; N, 6.3%.

2.3.2. Preparation of $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(bpmk)]PF_6$ (**5b**)

The complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2(CH_3CN)]PF_6$ (**1**) (100 mg, 0.107 mmol) and the ligand bpmk (63 mg, 0.26 mmol) were dissolved in minimum amount of CH_2Cl_2 and benzene (40 ml) was added. The resulting solution was heated to reflux for 10 h under nitrogen atmosphere. The solution became light brown color as reaction proceeded. A workup analogous with that of **5a** afforded the product as light brown solid. Yield: 69 mg, 75%.

NMR (δ_H,$CDCl_3$): 9.48 (d, 1H, ^3J(HH) = 5.8), 9.28 (d, 1H, ^3J(HH) = 4.2), 8.59 (d, 1H, ^3J(HH = 3.8) 4.12), 8.77(d, 1H, ^3J(HH) = 4.12), 8.59(d, 1H, ^3J(HH) = 3.8) 8.17(t, 1H, ^3J(HH) = 4.9), 7.92 (t, 1H, ^3J(HH) = 7.8), 7.62(t, 1H, ^3J(HH) = 7.5), 7.52 (t, 1H, ^3J(HH) = 4.32), 6.99–7.40 (m, 18H), 4.95 (d, 2H, ^3J(HH) = 3.8), 4.47 (t, 1H, ^3J(HH) = 2.9), 2.34 (s, 3H), 2.29 (s, 3H). NMR (δ_P, $CDCl_3$): 55.43. IR (KBr, cm^{-1}): 1633, 1620 $\nu_{(C=N)}$, 844 $\nu_{(PF6)}$. Anal. Calc. for $C_{41}H_{36}N_4P_2F_6Ru$: C, 57.13; H, 4.18; N, 6.50. Found: C, 57.76; H, 4.36; N, 6.13%. UV–visible (λ_{max}, nm): 447.

2.3.3. $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(bpk)]BF_4$ (**5c**)

This complex was prepared in analogy to the preparation of (**5a**), except the complex $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2(CH_3CN)]BF_4$ (**4**) was used instead of complex (**3**).Yield: 68 mg, 76%.

NMR (δ_H, $CDCl_3$): 8.93 (d, 1H, ^3J(HH) = 6), 8.79 (d, 1H, ^3J(HH) = 5.13), 8.36 (s, 1H), 8.16 (s, 1H), 8.08 (s, 1H), 8.08 (d, 1H, ^3J(HH) = 2.34), 7.69 (dt, 1H, J(HH) = 1.28, ^4J(HH) = 12.8), 7.64 (dt, 1H, ^3J(HH) = 1.84, ^4J(HH) = 15.3), 7.49 (br, 1H), 7.43 (br, 1H), 6.84–7.36 (m, 15H), 1.45 (d, 15H, ^4J(HP) = 1.18, (C_5Me_5)). NMR (δ_P, $CDCl_3$): 46.92. IR (KBr, cm^{-1}): 1619, 1608 $\nu_{(C=N)}$, 1082 $\nu_{(BF_4)}$. Anal. Calc. for $C_{40}H_{40}BF_4N_4PRu$: C, 60.33; H, 5.02; N, 7.03. Found: C, 59.26; H, 4.98; N, 7.24%. UV–vis (λ_{max}, nm): 455.

2.3.4. $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(bpmk)]BF_4$ (**5d**)

This complex was prepared similar to (**5b**), except the complex $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2(CH_3CN)]BF_4$ (100 mg, 0.12 mmol) was used instead of complex **3** and refluxed for 10 h. Following the same procedure as for complex (**5b**), the complex (**5d**) was obtained as a light brown solid. Yield: 66 mg, 72%.

NMR (δ_H, $CDCl_3$): 9.04(d, 1H, ^3J(HH) = 5.14), 8.76 (d, 1H, ^3J(HH) = 4.70), 8.67 (d, 1H, ^3J(HH) = 5.21), 8.15 (d, 1H, ^3J(HH) = 1.97), 7.93 (dt, 1H, ^3J(HH) = 1.9, ^4J(HH) = 15.9), 7.72 (br, 1H), 6.84–7.64 (m, 17H), 2.29 (s, 3H), 2.14 (s, 3H), 1.45 (d, 15H, ^4J(HP) = 1.37, C_5Me_5). NMR (δ_P, $CDCl_3$): 46.36. IR (KBr, cm^{-1}): 1624, 1612 $\nu_{(C=N)}$, 1082 $\nu_{(BF_4)}$. Anal. Calc. for $C_{42}H_{44}BF_4N_4PRu$: C, 61.19; H, 5.34; N, 6.79. Found: C, 60.37; H, 5.18; N, 6.28%. UV–vis (λ_{max}, nm): 425.

2.3.5. Preparation of $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(pdk)]PF_6$ (**6a**)

The complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2(CH_3CN)]PF_6$ (100 mg, 0.12 mmol) and the ligand pdk (63 mg, 0.22 mmol) were dissolved in minimum amount of dichloromethane (5 ml) and then benzene (40 ml) was added. The resulting mixture was heated to reflux for 10 h under nitrogen atmosphere. The color of the solution progressively changed from yellow orange to dark brown. After the mixture was cooled, the solvent was removed by rotary evaporator. The brown residue was extracted with CH_2Cl_2 and purified by column chromatography on silica gel using dichloromethane: acetone (8:1, v/v) mixture as an eluent. The solution was concentrated to ca. 5 ml and addition of excess hexane gave the compound **6a** as dark brown solid. The brown solid was collected and washed with hexane. Yield: 73 mg, 75%.

NMR (δ_H, $CDCl_3$): 9.59 (s, 1H, NH), 8.85 (d, 1H, ^3J(HH) = 3.92), 8.11(s, 1H), 7.99 (d, 1H, ^3J(HH) = 4.7), 7.84 (dt, 1H, ^3J(HH) = 1.5, ^4J(HH) = 15), 7.58 (dt, 1H, ^3J(HH) = 1.08, ^4J(HH) = 12), 6.82–7.50 (m, 22H), 5.52 (d, 2H,^3J(HH) = 3.6, indenyl) 4.71(t, 1H, ^3J(HH) = 4.2, indenyl). NMR (δ_P, $CDCl_3$): 47.82. IR (KBr, cm^{-1}): 1606 $\nu_{(C=N)}$, 1493 $\nu_{sym(NO_2)}$, 1341 $\nu_{asym(NO_2)}$, 844 $\nu_{(PF_6)}$. UV–vis (λ_{max}, nm): 423. Anal. Calc. for $C_{39}H_{31}F_6N_5O_4P_2Ru$: C, 51.38; H, 3.40; N, 7.68. Found: C, 51.86; H, 3.86; N, 7.25%.

*2.3.6. Preparation of [(η^5-C_9H_7)Ru(PPh_3)(pdmk)]PF_6 (**6b**)*

The complex was prepared by analogy to that of **5b**, using the complex [(η^5-C_9H_7)Ru(PPh_3)$_2$(CH_3CN)]PF_6 (100 mg, 0.11 mmol) and the ligand, pdmk (69 mg, 0.22 mmol) and isolated as light brown solid. Yield: 70 mg, 71%.

NMR (δ_H, $CDCl_3$): (Signals for the minor isomer are given in the parentheses). 10.42 (9.96) (s, 1H, NH), 9.33 (9.22) (d, 1H, 3.8, ^3J(HH) = 2.44), 8.79* (d, 1H, ^3J(HH) = 2.59), 8.41 (dt, 1H, J(HH) = 1.8, ^4J(HH) = 11.46), 7.66–6.86* (m, 23H), 5.10 (4.99) (d, 2H, ^3J(HH) = 4.32, 2.43, indenyl), 4.74 (4.50) (t, 1H, unresolved, indenyl), 2.62 (2.38) (s, 3H). *Signals for the minor isomer are obscured by the major isomer. NMR (δ_P, $CDCl_3$): 47.53. IR (KBr, cm^{-1}): 1613 $\nu_{(C=N)}$, 1513 $\nu_{asym(NO_2)}$, 1334 $\nu_{sym(NO_2)}$, 844 $\nu_{(PF_6)}$. Anal. Calc. for $C_{40}H_{33}F_6N_5O_4P_2Ru$: C, 51.94; H, 3.57; N, 7.57. Found: C, 52.12; H, 3.86; N, 7.15%. UV–vis ($\lambda_{max,}$ nm): 418.

*2.3.7. Preparation of [(η^5-C_5Me_5)Ru(PPh_3)(pdk)]BF_4 (**6c**)*

This complex was prepared by following the same procedure as (**6a**) except the complex [(η^5-C_5Me_5)Ru(PPh_3)$_2$(CH_3CN)]BF_4 (**4**) was used in place of [(η^5-C_9H_7)Ru(PPh_3)$_2$(CH_3CN)]PF_6 (**3**). Yield: 69 mg, 70%.

NMR (δ_H, $CDCl_3$): 9.62 (s, 1H, NH), 8.91 (d, 1H, ^3J(HH) = 4.8), 8.54 (s, 1H) 8.31 (dt, 1H, ^3J(HH) = 1.9, ^4J(HH) = 9.8), 8.12 (dt, 1H, ^3J(HH) = 4.2, ^4J(HH) = 6.2), 6.92–7.94 (m, 19H), 1.36 (s, 15H, C_5Me_5). NMR (δ_P, $CDCl_3$): 42.74. IR (KBr, cm^{-1}): 1623 $\nu_{(C=N)}$, 1497 $\nu_{asym(NO_2)}$, 1348 $\nu_{sym(NO_2)}$. Anal. Calc. for $C_{40}H_{39}BF_4N_5PRu$: C, 55.04; H, 4.47; N, 8.02. Found: C, 54.21; H, 4.86; N, 7.89%. UV–vis ($\lambda_{max,}$ nm): 416.

*2.3.8. Preparation of [(η^5-C_5Me_5)Ru(PPh_3)(pdmk)]BF_4 (**6d**)*

The same procedure as (**6b**) was adopted except the complex [(η^5-C_5Me_5)Ru(PPh_3)$_2$(CH_3CN)]BF_4 was used in place of [(η^5-C_9H_7)Ru(PPh_3)$_2$(CH_3CN)]PF_6. Yield: 73 mg, 74%.

NMR (δ_H, $CDCl_3$): 9.24 (s, 1H, NH), 8.52 (d, 1H, ^3J(HH) = 3.8), 8.23 (t, 1H, ^3J(HH) = 4.3), 8.12 (t, 1H, ^3J(HH) = 3.8), 6.89–7.84 (m, 19H), 2.34 (s, 3H),1.34 (d, 15H, ^4J(HP) = 1.23, C_5Me_5). NMR (δ_P, $CDCl_3$): 42. 63. IR (KBr, cm^{-1}): 1625 $\nu_{(C=N)}$, 1491 $\nu_{asym(NO_2)}$, 1348 $\nu_{sym(NO_2)}$. Anal. Calc. for $C_{41}H_{41}BF_4N_5PRu$: C, 55.52; H, 4.62; N, 7.90. Found: C, 54.98; H, 5.06; N, 7.28%. UV–vis ($\lambda_{max,}$ nm): 433.

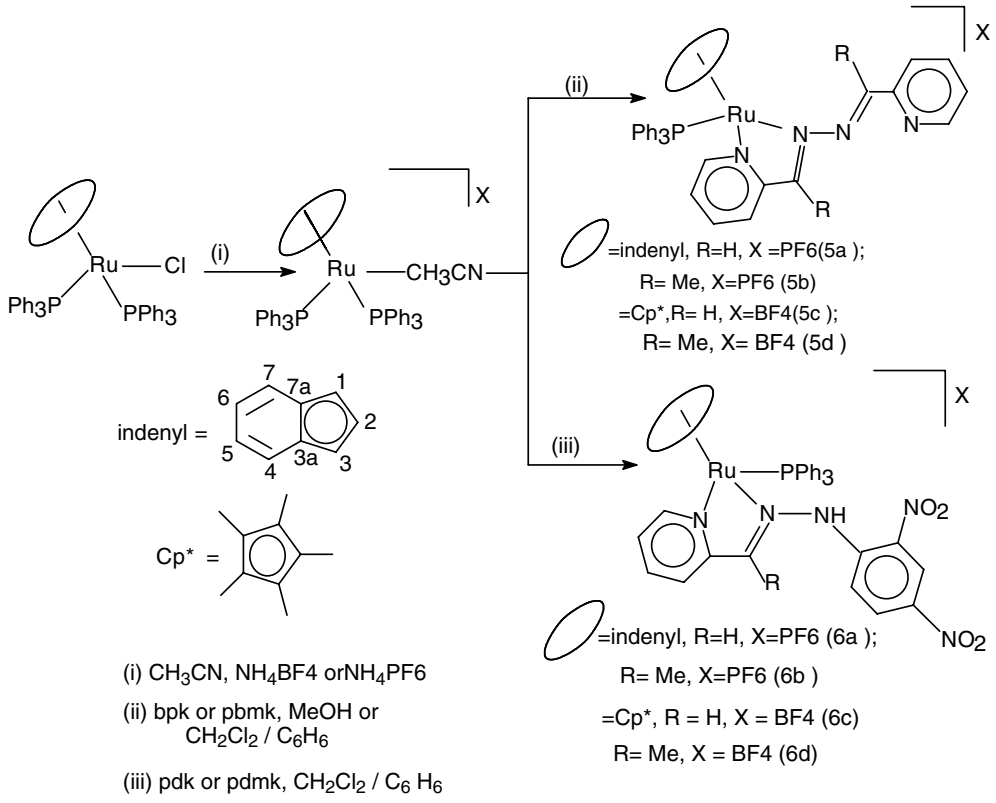
3. Structure analysis and refinement

X-ray quality crystals of both the complexes **5c** and **6a** were grown by slow diffusion of hexane into dichloromethane solution of **5c** and **6a**. The X-ray intensity data were measured at 293(2) K for complex **5c** and 133(2) K for complex **6a** respectively measured on a Smart Apex with CCD detector and Bruker Smart 1000 CCD detector, respectively employing graphite monochromater using Mo Kα radiation (λ = 0.71073 Å). Intensity data were corrected for Lorentz and polarization effects and absorption correction was made using SAINT program [25]. The structures were solved by direct methods (SHELXS 97) [26] and refined by full matrix least squares base on F^2 using (SHELXL-97) [27]. The weighting scheme used. $W = 1/[\sigma^2(F_o^2) + aP^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a "riding" model. Refinement converged at a final R = 0.0421 and 0.0352 for complex **5c** and **6a**, respectively, (for observed data F), and wR_2 = 0.1057 and 0.07909 for complex **5c** and **6a** respectively, (for unique data F^2).

4. Results and discussion

The reaction of [(η^5-C_9H_7)Ru(PPh_3)$_2$(CH_3CN)]PF_6 (**3**) or [(η^5-C_5Me_5)Ru(PPh_3)$_2$(CH_3CN)]BF_4 (**4**) with the azine ligands viz., bpk or bpmk in refluxing methanol or dichloromethane/benzene mixture gives mononuclear complexes (**5a**–**5d**) in good yield (72–78%) as the only product irrespective of the stoicheometric ratios (Scheme 2). Although some dinuclear complexes of similar ligands were reported in arene ruthenium(II) cases [20], our attempt to synthesize dinuclear complexes of indenyl and pentamethylcyclopentadienyl were unsuccessful probably due to the presence of satirically demanding triphenylphosphine ligand. In similar manner, the reaction of complex (**3**) or (**4**) with pdk or pdmk in refluxing dichloromethane/benzene mixture leads to the formation of the complexes (**6a**–**6d**) in good yield. The complexes were purified by column chromatography technique and obtained in 70–75% yield (Scheme 2). However, use of refluxing methanol as the reaction medium in the preparation of these complexes (**6a**–**6d**) afforded a green compound. Spectroscopic data suggest that the green compound could be ambiguously a decomposed product as evident from the absence of the characteristic signals of indenyl and Cp* ligand in the proton NMR spectrum. The exact structure of the compound is yet not known, the investigation is under progress. All these complexes (**6a**–**6d**) are air stable in solid state and soluble in chlorinated solvents. They have been characterized by microanalyses, infrared and NMR (^1H, ^{31}P {^1H}) spectroscopy (details are given in Section 2) and X-ray diffraction study for representative complexes **5c** and **6a** have been carried out.

The IR-spectra of the complexes showed absorption bands in the region of 1606–1633 cm^{-1} corresponding to the $\nu_{C=N}$ stretching frequency of the ligands. The complexes **5a**–**5d** exhibits two absorption bands, one at



Scheme 2.

a lower frequency which could be assignable to the coordinated $\nu_{C=N}$ while other at a little higher frequency assignable to the uncoordinated $\nu_{C=N}$ frequency. The spectra also contained absorption bands for the PF_6 and BF_4 counter anions at 844 and 1082 cm^{-1}, respectively. A strong band was observed in the IR spectra of the complexes **6a**–**6d** in the region 1491–1513 cm^{-1} corresponding to the ν_{NO_2} (asymmetric stretching vibration) while for the symmetric stretching vibration the band is observed in the region 1334–1348 cm^{-1}. The proton NMR spectra of these complexes showed the resonances for the indenyl and Cp* ligands, apart from the signals for the coordinated azine ligand and triphenylphosphine.

The spectra of the Cp* complexes showed resonance for the methyl protons of the Cp* ligand as singlet and occasionally doublet as previously found in other Cp* complexes [15,16b] in the range of δ 1.35–1.45. The doublet observed could be due to the coupling of the proton of the methyl group with the phosphorous atom of the triphenylphosphine. As have been observed in some other indenyl complexes [14a], in the proton NMR spectra of the indenyl complexes, the resonances for the $H^{1,3}$ protons was found to be shift in the up field region relative to the H^2 proton, where the protons of $H^{1,3}$ observed as a doublet in the range of δ 4.95–5.52 [J(HH) = 2.1–3.8 Hz] and that of H^2 in the range of δ 4.47–4.74 [J(HH) = 2.9–4.2 Hz], respectively (occasionally as two unresolved multiplets). However, the reverse was observed in the indenyl ruthenium allenylidene and Schiff's base complexes [14b,16a]. The up field shift of H^2 proton could be due to the slight distortion towards η^3-mode in these complexes. The distortion towards η^3 mode leads to the greater localization of electron around H^2 and consequently the proton is well shielded as compared to the protons of $H^{1,3}$. Further, the proton NMR spectra of these complexes exhibit a doublet at δ 8.52–8.93 in the cases of Cp* complexes while at a lower field strength in the range of δ 9.22–9.80 in the case of indenyl complexes which are assignable to the *ortho* protons of the pyridine of the ligand. The complexes (**6a**–**6d**) display the signals for NH proton of the ligand. In the indenyl complexes this NH proton were observed at down field region at δ 9.59 and 10.42 as compared to Cp* complexes where the resonance were observed at δ 9.32 and 9.24, respectively. The proton NMR spectra of all these complexes exhibit a multiplet resonance in the range of δ 6.69–7.94 corresponding to the protons of arene and triphenylphosphine ligands. The proton NMR spectra of representative complexes **5a** and **6b** are shown in Fig. 1.

The complexes may exhibit diasteriomerism, but all efforts to separate the diasteriomers were unsuccessful in our working condition. However, the existence of

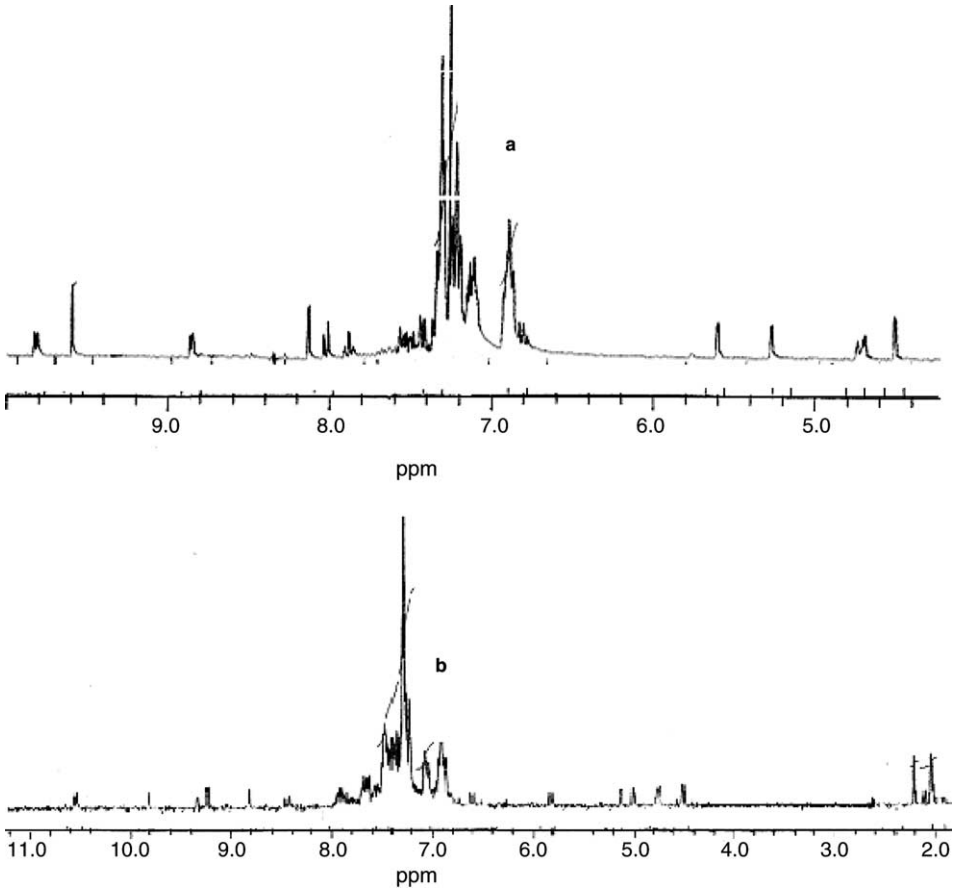


Fig. 1. ^{1}H NMR spectrum of (a) complex **5a** (b) complex **6b.**

diasteriomers has been supported by the ill resolved NMR data. The complex (**6b**) exhibit diasteriomers in the ratio 1:1.7. Except complex (**6b**), in the respective spectra of the complexes, signals for the minor diasteriomers is hidden or not well resolved, therefore, we are unable to make precise interpretation of the different signals. In this communication, except (**6b**), in the rest of the complexes we have taken into account only for the major isomers. In the spectrum of complex **6b** the major isomer resonances appeared in the downfield region with comparison to the minor isomer. The ^{31}P $\{^{1}H\}$ spectra of the indenyl complexes (**5a**) and (**5b**) appeared in the down field region at δ 55.84 and 55.43, respectively as compared to the analogous Cp* complexes (**6a**) and (**6b**) where the resonance appeared at δ 47.8 and 47.5, respectively. The most remarkable features of the ^{31}P $\{^{1}H\}$ NMR spectra is the up field shift of the resonances of the nitro substituted azine complexes in both indenyl and Cp* complexes relative to the starting precursor complexes **3** and **4**. The signals for the indenyl complexes (**6a**) and (**6b**) are observed at δ 47.8 and 47.5 while for the Cp* complexes (**6c**) and (**6d**) at δ 42.74 and 42.63, respectively. The UV–visible spectra of the complexes in CH_2Cl_2 at ca. 10^{-4} M showed absorption band in the range of 416–456 nm. This low energy band is assignable to metal to ligand charge transfer transition (MLCT), [Ru(dπ)–L(pπ)] (Fig. 2).

5. Crystal structures determination

The crystal structures determination were carried out for the representative complexes **5c** and **6a**. The perspective views of each complex including atom numbering schemes are shown in Figs. 3 and 4. Details of crystallographic data collection parameters are summarized in Table 1. Selected bond lengths and bond angles are listed in Tables 2 and 3.

The complex **5c** crystallize in the space group *P*1. There are two independent molecules, A and B in the triclinic unit cell which are mirror images to each other. The geometry around the ruthenium atom can be regarded as distorted octahedral 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 PPh_3 and N-atoms of the coordinated azine ligand. The centroid bond distance between the ruthenium and ring carbons is 1.853 Å (molecule A)

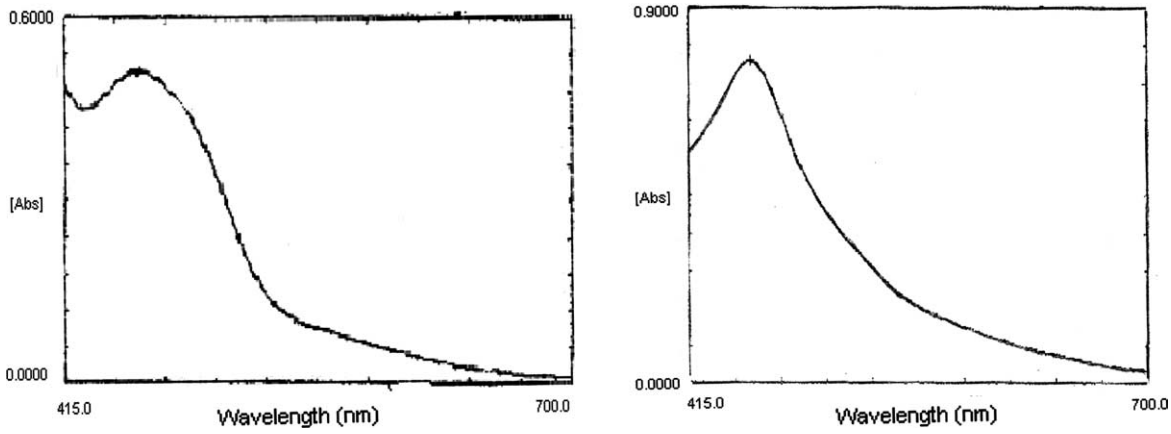


Fig. 2. UV–visible spectra of complex **5a** and **5c**. UV–visible spectrum of complex **5a** in CH_2Cl_2. UV–visible spectrum of complex **5c** in CH_2Cl_2.

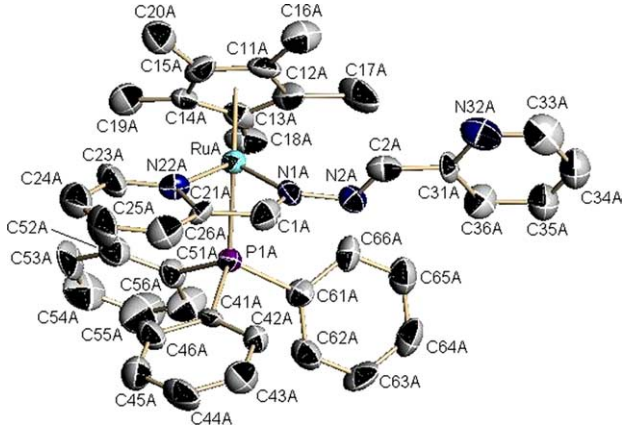


Fig. 3. Molecular structure of complex $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(C_5H_4N\text{–}CH{=}N\text{–}N{=}CH\text{–}C_5H_4N)]BF_4$ (**5c**) with 50% probable thermal ellipsoids. Hydrogen atoms and BF_4 ion have been omitted for clarity.

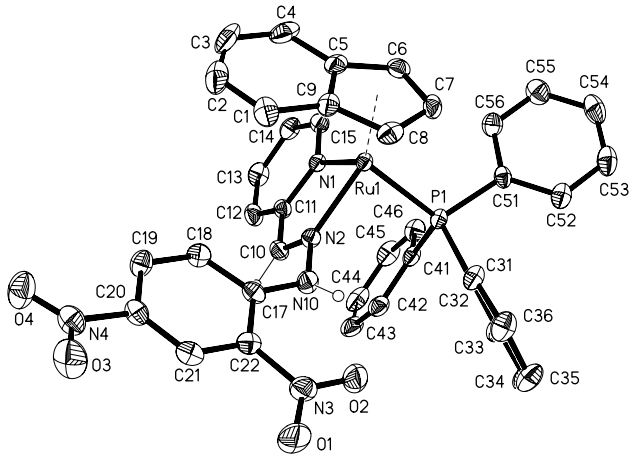


Fig. 4. Molecular structure of complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)\{C_5H_4N\text{–}CH{=}N\text{–}NH\text{–}C_6H_3(NO_2)_2\}]PF_6$ (**6a**) showing with 50% probable thermal ellipsoids. Hydrogen atoms and PF_6 ion have been omitted for clarity.

and 1.852 Å (molecule B) which are comparable to that observed in the related Cp* complex [16b]. Interestingly, all the C–C bond lengths in the five member ring are equal to 1.4200 Å, which suggests a considerable delocalization of π-electron in the ring. The Ru–P bond length 2.344(2) Å is comparable to that found in related Ru–PPh_3 complex (2.3593(7) Å) [16b] but longer to that of complex **6a** and other indenyl ruthenium complexes. The higher value of Ru–P bond distance in Cp* complexes could be due to the bulkiness of the Cp* ligand. Further, five member ring is planar as evident by the nearly equal bond distances between the ruthenium atom and the ring carbons. The bpk ligand is coordinated by two N-atoms giving rise to the formation of five member metallacycle. The five member metallacycle is being planarity with that of the Cp* ligand and they are in *cis* position with respect to each other while the uncoordinated pyridyl ring is slightly twisted out of the plane. The bite angle of the chelating ligand N(1A)–Ru–N(22A) is 75.9(2)° which is very close to that found in the other related complex [16b]. The C=N bond length of the coordinated nitrogen, N(1A)–C(1A) (1.270 (13) Å) is longer than that of the uncoordinated C=N, N(2A)–C(2A) (1.210 (12) Å) which could be due to the back donation of electron from metal to π* orbital of the ligand.

The complex **6a** crystallize in the $Pca2_1$ space group. As in complex **5c** the unit cell contains two independent cations and anions (molecules 1 and 2). The centroid bond distance between ruthenium and ring carbons for the two molecules are Ru1–C_9H_7 (1.8571(12)) and Ru2–C_9H_7 (1.8530(12)) Å, respectively. The indenyl ligand in the complex is bonded to η^5-fashion and displays the asymmetric coordination generally observed with this ligand [28]. The indenyl ligand exhibits a pronounced "slip-fold" (Δ) distortion [29] relative to a planar, the value being 0.1045 Å which is comparable to that found in other indenyl complexes [16a]. The η^5-indenyl ligand is distorted from planar, such that the

Table 1
Summary of structure determination of complex **5c** and complex **6a**

Empirical formula	$C_{40}H_{40}BF_4N_4PRu$	$C_{39}H_{31}F_6N_5O_4P_2Ru$
Formula weight	795.61	910.70
Temperature (K)	293(2)	133(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	*P*1	$Pca2_1$
Unit cell dimensions		
a (Å)	9.3834(5)	34.395(3)
b (Å)	11.2553(6)	11.2596(8)
c (Å)	17.7894(10)	19.3674(14)
α (°)	95.5400(10)	90°
β (°)	92.8020(10)	
γ (°)	93.9930(10)	
Volume (Å^3)	1862.55(18)	7500.5(9)
Z	2	8
Density (calculated) (mg/m^3)	1.419	1.613
Absorption coefficient (mm^{-1})	0.518	0.583
F(000)	816	3680
Crystal size (mm^3)	$0.25 \times 0.35 \times 0.40$	$0.31 \times 0.28 \times 0.19$
θ range for data collection	1.82–28.30°	1.18–30.04°
Index ranges	$-11 \leqslant h \leqslant 12$, $-14 \leqslant k \leqslant 14$, $-22 \leqslant l \leqslant 22$	$-48 \leqslant h \leqslant 48$, $-15 \leqslant k \leqslant 15$, $-27 \leqslant l \leqslant 27$
Reflections collected	16,404	147,107
Independent reflections	14,630 [*R*(int) = 0.0122]	21,929 [*R*(int) = 0.0656]
Completeness to theta	=28.30°, 91.4%	30.00°, 100.0%
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	14,630/3/744	21,929/1/1035
Goodness-of-fit on F^2	1.036	1.051
Final *R* indices	$R_1 = 0.0421$	$R_1 = 0.0352$,
[*I*>2sigma(*I*)]	$wR_2 = 0.1057$	$wR_2 = 0.0709$
R indices (all data)	$R_1 = 0.0481$, $wR_2 = 0.1110$	$R_1 = 0.0519$, $wR_2 = 0.0774$
Absolute structure parameter	0.0(7)	−0.003(12)
Largest different peak and hole (e Å^{-3})	0.848 and −0.471	0.865 and −0.410

Table 2
Selected bond lengths (Å) and angles (°) of complex **5c**

Bond lengths	
RuA–C*	1.853 Å
RuA–N(1A)	2.073(7)
RuA–N(22A)	2.084(2)
RuA–P(1A)	2.344(2)
N(1A)–N(2A)	1.402(10)
N(1A)–C(1A)	1.270(13)
N(2A)–C(2A)	1.210(12)
Bond angles	
N(1A)–RuA–N(22A)	75.9(2)
N(1A)–RuA–P(1A)	89.6(2)
N(22A)–RuA–P(1A)	90.34(8)
C(1A)–N(1A)–N(2A)	117.7(8)
C(1A)–N(1A)–RuA	118.2(6)
N(2A)–C(2A)–C(31A)	122.8(9)

C* = Centroid of C(11A), C(12A), C(13A), C(14A), C(15A).

Ru1–C bond distances of bridging carbon atoms Ru1–C(5) (2.2902(7)) and Ru1–C(9) (2.285(3)) Å are longer than those to the "allylic" carbons Ru1–C(6) (2.188(3)), Ru1–C(7) (2.171(3)), Ru1–C(82.183(3)) Å. The asymmetric Ru–C bond lengths are also observed in other indenyl ruthenium complexes [14,16a,17a]. The asymmetric metal carbon bond distance is due to the slipping of ruthenium across the η^5- to η^3-coordination [28]. Although indenyl ligand is η^5-bonded to the metal atom, the structure shows a slight distortion of the five member ring from planarity [30]. In contrast, the benzo ring of the indenyl ligand is planar and show significant localization of double bond at the C(1)–C(2) (1.357(5) Å), C(3)–C(4) (1.371(5) Å) as previously found for other indenyl complexes [14a,14b,16a,17a]. Both these bond lengths are significantly shorter than those of other three bonds viz. C(2)–C(3) (1.399(6) Å), C(1)–C(9) (1.420(4) Å), and C(5)–C(4) (1.419(4) Å) in the benzo ring. On the other hand, there is a delocalization of π-electrons in the five member ring as evident from the nearly equal bond lengths between the C–C bond distances of the five member ring, the bond lengths falls within the range of 1.422(4)–1.444(4) Å. The Ru1–P1 bond distance 2.2902(7) Å is comparable to that of other related indenyl ruthenium complexes [16a,17a], but little shorter than that of the complex **5c** and other Cp* complexes [16b]. The molecule exhibits the well known pseudo-octahedral piano-stool geometry. The inter ligand angles P(1)–Ru1–N(1), P(1)–Ru1–N(2), N(1)–Ru1–N(2) and those between centroid and the legs

Table 3
Selected bond lengths (Å) and bond angles (°) of the complex **6a** including hydrogen bond

Bond lengths	
Ru1–C**	1.8571(12)
Ru1–N(1)	2.097(2)
Ru1–N(2)	2.052(2)
Ru1–P(1)	2.2902(7)
N(2)–N(10)	1.407(3)
N(2)–C(10)	1.304(3)
C(5)–C(6)	1.433(4)
C(6)–C(7)	1.424(4)
C(7)–C(8)	1.422(4)
Ru1–C(5)	2.2902(7)
Ru1–C(6)	2.188(3)
Ru1–C(7)	2.171(3)
Ru1–C(8)	2.183(3)
Ru1–C(9)	2.285(3)
C(8)–C(9)	1.442(4)
C(9)–C(5)	1.444((4)
N(10)–H(0A)···O(2)	2.596(3)
Bond angles	
N(2)–Ru(1)–N(1)	75.53(8)
N(2)–Ru(1)–P(1)	89.10(7)
N(1)–Ru(1)–P(1)	92.90(6)
N(10)–H(0A)···O(2)	131(3)
C(10)–N(2)–N(10)	115.4(2)
N(2)–C(10)–C(11)	115.6(2)
C(17)–N(10)–N(2)	122.6(3)

C** = Centroid of C(5), C(6), C(7), C(8), C(9).

show typical of a pseudo-octahedron geometry. As observed in other indenyl ruthenium complexes [14a,16a,17a] the structure showed *cis* orientation of the benzo ring of the indenyl ligand with respect to the coordinated azine ligand. The N–N bond length of N(2)–N(10) (1.407(3) Å) is comparable to that of complex **5c** (1.402(10) Å) (Tables 2 and 3). There is hydrogen bonding between the hydrogen of the NH group and the oxygen of the ortho nitro group (N(10)–H–O_2) of the pdk ligand (Table 3).

Acknowledgement

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Appendix A. Supplementary data

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre (CCDC), CCDC No. 266103 for complex **5c** and CCDC No. 266104 for complex **6a**. 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.jorganchem.2005.05.001.

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