Reactivity Studies of η^5 - Indenyl and η^5 -Cp* Ruthenium(II) Complexes towards some Polypyridyl Ligands

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Abstract. The reaction of $[(\eta^5-L^3)Ru(PPh_3)_2Cl]$, where; $L^3 = C_9H_7$ (1), C_5Me_5 (Cp*) (2) with acetonitrile in the presence of $[NH_4][PF_6]$ yielded cationic complexes $[(\eta^5-L^3)Ru(PPh_3)_2(CH_3CN)][PF_6]; L^3 =$ C_9H_7 ([3]PF₆) and $L^3 = C_5Me_5$ ([4]PF₆), respectively. Complexes $[3]PF_6$ and $[4]PF_6$ reacts with some polypyridyl ligands viz, 2,3bis (α -pyridyl) pyrazine (bpp), 2,3-bis (α -pyridyl) quinoxaline (bpq) vielding the complexes of the formulation [(η⁵- L^{3})Ru(PPh₃)(L^{2})]PF₆ where; $L^{3} = C_{9}H_{7}$, $L^{2} = bpp$, ($/5/PF_{6}$), $L^{3} =$ C_9H_7 , $L^2 = bpq$, (/6/PF₆); $L^3 = C_5Me_5$, $L^2 = bpp$, (/7/PF₆) and bpq, $(/8/PF_6)$, respectively. However reaction of $[(\eta^5 C_9H_7$ Ru(PPh₃)₂(CH₃CN)[PF₆] (/3/PF₆) with the sterically demanding polypyridyl ligands, viz. 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) or tetra-2-pyridyl-1,4-pyrazine (tppz) leads to the formation of unexpected complexes $[Ru(PPh_3)_2(L^2)(CH_3CN)][PF_6]_2$; $L^2 =$ tppz ($[9](PF_6)_2$), tptz ($[11](PF_6)_2$) and $[Ru(PPh_3)_2(L^2)Cl][PF_6]$; $L^2 =$ tppz ($[10]PF_6$), tptz ($[12]PF_6$). The complexes were isolated as their hexafluorophosphate salts. They have been characterized on the basis of micro analytical and spectroscopic data. The crystal structures of the representative complexes were established by Xray crystallography.

Keywords: Ruthenium; Indenyl; Crystal structure; Triazine; Pyrazine

1 Introduction

Cyclopentadienyl ruthenium(II) bisphosphine complexes $[Cp'Ru(PPh_3)_2Cl]$ (Cp' = Cp, Cp*, indenyl) have been immense interest owing to their high reactivity [1], catalytic activity [2] and interesting reactions towards some terminal alkynes [3, 4]. An extensive studied have been carried out on the cyclopentadienyl bisphosphine ruthenium complexes [5-7]. In contrast, the analogous indenyl and Cp^{*} complexes have not been much studied. Literature survey reveals that most of the reaction on indenyl and Cp*ruthenium(II) phosphine complexes $[(\eta^5-C_9H_7)Ru(L)_2Cl]$ (where, $L = PPh_3$, PMe₂Ph, PMePh₂) are centered on the reactions towards terminal acetylenes [3, 4]. However, the reaction of the complex $[(\eta^5\text{-}L^3)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ with N-base ligands are virtually unknown except a few report of such complexes appeared in the recent years [8]. It is noteworthy that complexes of indenyl and Cp* are differ from the analogous cyclopentadienyl complexes in certain aspects such as higher reactivity and labile nature of the organic moieties. The higher reactivity of indenyl complexes is attributed to the ring slippage nature from η^5 - to η^3 - and back to η^5 of the indenyl ligand [9].

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We had earlier reported the syntheses of indenyl, pentamethylcyclopentadienyl ruthenium complexes containing N, N donor Schiff's base [10] and azine ligands [11]. In continuation of our study, here we wish to report the reaction of $[(\eta^5-C_9H_7)Ru(PPh_3)_2(CH_3CN)][PF_6]$ (/3/PF₆) and $[(\eta^5-C_9H_7)Ru(PPh_3)_2(CH_3CN)][PF_6]$ C_5Me_5 Ru(PPh₃)₂(CH₃CN)][PF₆] (/4/PF₆) with some polypyridyl ligands viz, 3-bis (α-pyridyl) pyrazine (bpp), 2,3-bis (α-pyridyl) quinoxaline (bpq), 2,4,6-tris(2-pyridyl)-1,3,5triazine (tptz), tetra-2-pyridyl-1,4-pyrazine (tppz). The ligands involve in the study are shown in scheme 1. In the case of reaction of $[\eta^5$ -CpRu(PPh₃)₂Cl] with tppz and tptz, we obtained the complexes of the type $[CpRu(PPh_3)(L^2)]^+$; $(L^2 = \text{tppz or tptz ligand})$, where the Cp ligand remain intact to metal [12]. In contrast, in this present study the reaction of $[(\eta^5-C_9H_7)Ru(PPh_3)_2(CH_3CN)][PF_6]$ (131PF6) with tppz or tptz ligand, we isolated unexpected complexes $[Ru(PPh_3)_2(L^3)(CH_3CN)]^{2+}$ and $[Ru(PPh_3)_2(L^3)(Cl)]^+$ $(L^3 = tppz \text{ or } tptz)$. The complexes were fully characterized by elemental analyses, ¹H, ³¹P{¹H} NMR spectroscopy. The molecular structures of the compound $([9](PF_6)_2)$ and $(12 PF_6)$ have been determined by X-ray crystallography.

2 Results and Discussion

2.1 Reaction of $([3]PF_6)$ or $([4]PF_6)$ with bpp and bpq

The reaction of $([3]PF_6)$ or $([4]PF_6)$ with excess of bpp or bpq ligand in refluxing methanol affords the complexes $[(\eta^5-L^3)Ru(PPh_3)(L^2)][PF_6]$ (scheme 2) as the only product



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Scheme 1

in quantitative yield. The complexes can also be prepared in dichloromethane:benzene mixture (1:10 v/v). The complexes are air stable in solid state and soluble in chlorinated solvents such as dichloromethane, chloroform, *etc.* The electronic spectra of the complexes in dichloromethane (*ca* 10^{-4}) show absorption bands in the region 490-510 nm. This low energy transition is assignable to metal to ligand {Ru ($d\pi \rightarrow (L\pi)$ } charge transfer transition (MLCT). The compounds were characterized on the basis of microanalyses and NMR spectroscopy. The microanalytical data of the complexes are well consistent with the proposed structures. The proton NMR spectra of the complexes exhibit resonance for aromatic protons and ligands apart from indenyl and Cp* protons which are consistent with the proposed structures.

The proton NMR of the complexes ($[5]PF_6$) and ($[7]PF_6$) display a triplet at δ 4.75 and δ 5.07 and a doublet at δ 4.54 and 4.97 for the proton of H-2 ($J_{\rm HH} = 2.74$ -3.42 Hz) and H-1,3 ($J_{\rm HH} = 2.16$ -2.84 Hz) of the indenyl ligand, respectively. A single resonance was observed at d



Scheme 2

1.33 in the complexes $(f6]PF_6)$ and $(f8]PF_6)$ corresponding to the protons of Cp* ligand. The resonances for the coordinated ligand and triphenylphosphine appeared in the range of δ 9.64-6.29. The ³¹P{¹H} NMR of the indenyl complexes were resonate at a lower field at δ 56.25 as compared to the analogous Cp* complexes where the signal appeared at δ 45.19. A septet observed at δ -142 ($J_{P-F} =$ 712 Hz) is assignable to the [PF₆]⁻ ion.

2.2 Reaction of ([3]PF6) with tppz and tptz

reaction of $[(\eta^5-C_9H_7)Ru(PPh_3)_2(CH_3CN)][PF_6]$ The $(/3/PF_6)$ with terakis-2- pyridyl-1,4- pyrazine (tppz) and 2,4,6-Tris(2-pyridyl)-1,3,5-triazine (tptz) are solvent dependent. The reaction of $(/3/PF_6)$ with tppz or tptz in refluxing methanol for 4 to 5 h afforded a coordination comformulation $[Ru(PPh_3)_2(tppz)(CH_3CN)]^{2+}$ pound of $([9](PF_6)_2)$ and $[Ru(PPh_3)_2(tptz)(CH_3CN)]^{2+}$ $([11](PF_6)_2)$, respectively as depicted in scheme 3. Under similar condition, reaction of $(/4/PF_6)$ with tppz or tptz did not obtained any characterizable product. Because of the ill resolved NMR data of these products we are unable to precise interpretation of the different signals in these complexes. However, a similar type of complexes as shown in scheme 3 seems to be obtained in this case also as evident from the pattern of NMR spectrum. The complexes $([9](PF_6)_2)$ and $([11](PF_6)_2)$ were obtained as a result of displacement of indenyl group by tppz or tptz ligands. There are some reports available on such displacement of organic moiety in half sandwich complexes. The most prominent example is *Berke* and coworkers work, where chelating diphosphines displaced cyclopentadienyl ligand [13]. It is notable that indenyl ligands are more prone to such displacement by sterically demanding ligands than the Cp ligand due to the known indenyl effect, that is partial decoordination to an η^3 -mode due to the gain of aromatic resonance energy of the adjacent six membered ring. Interestingly, use of dichloromethane and toluene mixture instead of methanol as reaction medium afforded a chlorination products $[Ru(PPh_3)_2(tppz)Cl]^+$ ([10]PF₆) and $[Ru(PPh_3)_2(tptz)Cl]^+$ ([12]PF₆) where the indenyl group have been displaced by the incoming ligand and subsequently chlorination of the product by the chlorine generated from the dichloromethane. It is possible that a coordinatively unsaturated or coordinatively labile complex may readily abstract a chlorine atom from dichloromethane to give chlorinated complex. It is also known that 16 valence electron complex [RuCl(dppe)₂]⁺ revert to the corresponding dichloride [RuCl₂(dppe)₂] when kept in CH₂Cl₂ and the acetonitrile complex, $[Ru(dppm)_2Cl(CH_3CN)]^+$ when reduced in CH₂Cl₂ gives the cis and trans dichloride cis [Ru(dppm)₂Cl₂] and trans [Ru(dppm)₂Cl₂] [14].

Notably in our previous studies, we had described the reaction of $[CpRu(PPh_3)_2Cl]$ with tppz and tptz lignad to gave complex of the type $[CpRu(PPh_3)(L^2)]^+$; $L^2 = tppz$ or tptz ligand, where the Cp ligand remain intact to the metal atom [12]. In contrast, in the present case our attempt to

indenyl syntheses corresponding complex $[(\eta^{5}$ ind)Ru(PPh₃)(L²)]⁺, by reacting complex ($[3]PF_6$) with tppz or tptz were unsuccessful instead we isolated complexes without the organic moiety $([9](PF_6)_2)$ $(/12/PF_6)$. This suggests a more labile nature of indenyl as compared to analogous cyclopentadienyl ligand that sterically demanding tppz or tptz ligand readily displaced it from the complex. However, our recent studies on the reaction of $(/3/PF_6)$ or $(/4/PF_6)$ with less steric N-base ligands such as bipyridine, phenanthroline [8] and NN[/] donor schiff base [10] and azine ligands [11] yielded corresponding Nchelated η^5 -indenyl and η^5 -Cp* ruthenium complexes. This observation showed that steric factor of the ligand could play an important role in the stability of the indenyl moiety. It can be conclude that reaction of $(/3/PF_6)$ with less steric ligand does not displaced the indenyl group while with sterically demanding ligand displace indenyl group from the complex. The complexes $(/9/(PF_6)_2) - (/12/PF_6)$ were soluble in chlorinated solvents and they were isolated by column chromatography technique in fairly good yield as a major product. In each case a comparatively less quantity of minor product obtained were not characterized. The compounds were spectroscopically characterized and the structures of $([9](PF_6)_2)$ and $([12]PF_6)$ were confirmed by X-ray analyses. In the proton NMR spectra of the complexes the characteristic indenyl protons H² and H^{1,3} does not found indicating the absence of the indenvl ligand in the complex. Further, the proton NMR spectrum suggests the symmetrical coordination of this ligand to the metal atom *i.e.* three nitrogen chelate to the ruthenium atom. The resonance for the protons of the coordinated ligand and triphenylphosphine appeared in the range of δ 7.41-9.16. The ${}^{31}P{}^{1}H$ NMR spectra of the compounds showed a single resonance at δ 24.84 ([9](PF₆)₂), 24.98 ([10]PF₆), 28.62 $([11](PF_6)_2)$ and 13.80 $([12]PF_6)$, respectively. The most remarkable feature of the ³¹P{¹H} NMR spectra is the upfield shift of the resonance relative to the starting complexes $(3/PF_6)$ where the peak resonate at δ 48.29. The upfield shift could be due to the substitution of the indenyl ligand by the electron rich tppz or tptz ligands.

The electronic spectra of the complexes displayed three distinct peaks in the range of 430-495, 345-354 and 315-318 nm. The low energy bands at 430-495 nm has been assigned to MLCT transition {Ru $(d\pi \rightarrow (L\pi))$ } while the absorption bands below 400 nm were composed of second MLCT, ligand field or intra-ligand transitions $(\pi \rightarrow \pi^*)$. The analytical and spectroscopic data are well consisted with the formulation of these compounds. The electrochemical study of complex ($[12]PF_6$) was carried out in dry acetonitrile. The acetonitrile solution of ($[12]PF_6$) showed a quasireversible wave at -0.841 V ($\Delta E = 101.8$ mv) is assigned to the Ru^{II}-Ru^{III} couple [15].

3 Crystal Structures

Crystal structure determinations for the compound $([9](PF_6)_2)$ and $([12]PF_6)$ have been carried out. Details



(iii) tptz, MeOH (iv) tptz, CH2Cl2/ Toluene

Scheme 3

of crystallographic data collection parameters are summarized in Table 1. In this manuscript we present only the perspective view of the complex $([8]PF_6)$ (figure 1) to support the structure proposed by the spectroscopic data. In this molecule the unit cell contains two molecules, which are mirror images to each other. The centroid of Cp* ligand to ruthenium in the molecules are 1.849 and 1.864 Å, respectively. Due to not well defined of the atoms and poor quality of the crystals there is considerable error in the data and the refined R value is above 10 %, so the discussion about the crystal structure of this molecule $([8]PF_6)$ in the manuscript have been excluded.

3.1 Complex [Ru(PPh₃)₂(tppz)(CH₃CN)][PF₆]₂([9](PF₆)₂)

A perspective (ORTEP) [16] view of the complex cation along with the atoms numbering scheme is shown in figure 2. Selected bond lengths and angles are presented in Table 2. The compound $([9](PF_6)_2)$ crystallize in $P2_12_12_1$ space group in orthorhombic unit cell. The coordination of the ruthenium ion can be regarded as a distorted octahedron formed by the coordination of tppz in η^3 -fashion in a plane while the remaining coordination sites by the two tri-



Figure 1 Molecular structure of complex $(8[PF_6])$

phenylphosphine and acetonitrile ligand. It is notable that the uncoordinated pyridyl rings are slightly twisted out of the plane. The Ru-NCCH₃ bond distance Ru-N(1) (2.071(3) Å) is comparable to that of the other Ru-NCCH₃ bond length [10a]. The ruthenium to coordinated nitrogen bond distances Ru-N(22) ((2.0884) Å) and Ru-N(32) ((2.0717) Å), are comparable to those reported for Ru-nitrogen bond distances of tppz ligand [12]. The coordinated tppz ligand formed two five member metallacycle rings. The angle subtended by N(11)-Ru-N(22) and N(11)-Ru-N(32) are 78° and 79.9°, respectively. The Ru-PPh₃ bond distances, Ru-P(1) and Ru-P(2) is 2.4494(9) and 2.4185(9) Å which are in the usual range of Ru-P bond distance [17].



Figure 2 Molecular structure of the compound $[Ru(PPh_3)_2(tppz) (CH_3CN)][PF_6]_2$, $([9](PF_6)_2)$ showing with 50 % probable thermal ellipsoids. Phenyl rings of triphenylphosphine, hydrogen atoms and PF₆ ion have been omitted for clarity

3.2 Complex $[Ru(PPh_3)_2(tptz)Cl][PF_6]([12]PF_6)$

The complex crystallizes in $Pca2_1$ space group. There are two molecules (molecule **A** and molecule **B**) per unit cell. A perspective view of the cationic part of the molecule B with the atoms labeling scheme is shown in figure 3. Selected bond lengths and angles for both the molecules are listed

Table 1 Summary of structure determination for complex $([9](PF_6)_2)$ and $([12]PF_6)$

	Complex $[9](PF_6)_2$	Complex $[12]PF_6$
Empirical formula	$C_{62}H_{49}F_{12}N_7P_4Ru$	C ₅₄ H ₄₂ Cl F ₆ N ₆ P ₃ Ru
Formula weight	1345.03	1118.37
Temperature	293(2) K	183(2) K
Wavelength	0.71073 Å	0.71073 Å
Space group	P2 ₁ 2 ₁ 2 ₁	$Pca2_1$
Crystal system	orthorhombic	orthorhombic
Unit Cell dimension	$a = 11.2994(7) \dot{A}_{a}$	a = 31.886(6) Å
	$b = 23.1226(13) \dot{A}$	b = 17.505(3) Å
	c = 23.4581(13) Å	c = 18.145(3) Å
Volume	$6128.9(6) \text{ Å}^3$	10128(3) Å ³
Z	4	8
Density (calculated)	1.458 Mg/m ³	1.467 Mg/m ³
Absorption coefficient	0.442 mm^{-1}	0.523
F(000)	2728	4544
Crystal size	0.1 x 0.06 x 0.025 mm ³	0.04 x 0.03 x 0.03
Theta range for data collection	1.74 to 28.31°	1.16 to 16.05°
Index ranges	$-15 \le h \le 14$	$-24 \le h \le 24$
	$-30 \le k \le 30$	$-13 \le k \le 13$
	-30 < = 1 < = 31	$-14 \le 1 \le 13$
Reflections collected	53671	20324
Independent reflections	14481 [R(int) = 0.0305]	4906 [R(int) = 0.0575]
Completeness to theta	$= 28.31^{\circ}-96.9\%$	$= 16.05^{\circ}$ to 98.5 %
Absorption correction	Empirical	Empirical
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	14481 / 12 / 590	4906 / 13 / 342
Goodness-of-fit on F ²	1.006	1.073
Final R indices [I>2sigma(I)]	R1 = 0.0496, wR2 = 0.1300	R1 = 0.0857, wR2 = 0.2096,
R indices (all data)	R1 = 0.0555, wR2 = 0.1349	R1 = 0.0996, wR2 = 0.2228
Absolute structure parameter	-0.01(3)	0.45(11)
Largest diff. peak and hole	0.855 and $-0.526 \text{ e.}\text{\AA}^{-3}$	1.654 and $-0.590 \text{ e.}\text{\AA}^{-3}$

in Table 3 The molecule A and Molecule B differ in the orientation of the phenyl rings attached to the ruthenium atom arises due to twisted in different direction with respect to the rest part of the complex and also in the orientation of the pyridine ring. The pyridine rings in molecule B is twisted clockwise but in molecule A, it is twisted in counter clockwise as nitrogen atom is concerned. The ruthenium atom is hexa-coordinated with three coordination sites are occupied by the tptz ligand in η^3 -mode, while two sites by the P-atoms of the two triphenvlphosphine and the remaining one by the chlorine atom. The basal plane is formed by three nitrogen atoms N(11B), N(21B), N(31B) and one chlorine atom Cl(1B) which are coordinated to the ruthenium atom. Ru-N bond distances, Ru-N(31B) (2.145(5)), Ru-N(11B) (1.924(5)) A are in close agreement with those of the related compound [18]. The Ru-P bond length, Ru-P(1), (2.440(6)) and Ru-P(2), (2.402(6)) Å are similar with that of complex $(/9/(PF_6)_2)$. The Ru-Cl bond length 2.453(6) Å is in usual range of Ru-Cl bond length [19]. The coordinated tptz ligand forms two five member metallacycle ring in a plane with bite angles of N (31B)-RuB-N (11B) and N (21B)-RuB-N (11B) are 79.36(19)° and 77.53(19)°, respectively.

4 Experimental Section

The solvents were purified and dried by standard methods [20] and reactions were carried out under dry nitrogen atmosphere. The NMR spectra were recorded on Bruker ACF-300 and AMX-400 MHz spectrometer reference to external SiMe₄. The chemical shift for ${}^{31}P{}^{1}H$ NMR were recorded reference to H_3PO_4 (85%). Coupling constants are given in hertz. UV-visible was recorded on Hitachi-U-2300 spectrophotometer and Micro analytical data were obtained from SAIF NEHU, Shillong, using a Perkin Elmer 2400 CHN/S analyzer. The CV was recorded on CHI 6208 instruments Electrochemical analyzer in de-aerated acetonitrile in the presence of 0.1 M tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte, using three electrode assembly platinum working and counter electrodes and Ag/AgCl as reference electrode. The ligands 2,3-bis(α -pyridyl)pyrazine (bpp), 2,3-bis(α -pyridyl)quinoxaline (bpq), bis-pyridyl quinoxaline (bpq) and terakis pyridyl-1,4- pyrazine (tppz) were prepared by following a literature method [21] while the ligand 2,4,6-Tris(2-pyridyl)-1,3,5-triazine (tptz) was purchased from Loba Chemie (P) Ltd. and used as received. The starting materials, $[(\eta^5-C_9H_7)Ru(PPh_3)_2Cl]$ (1) [22] and $[(\eta^5-C_9H_7)Ru(PPh_3)_2Cl]$ (1) [22] and $[(\eta^5-C_9H_7)Ru(PPh_3)_2Cl]$ C_5Me_5 Ru(PPh₃)₂Cl] (2) [4] were prepared following the literature methods while the precursor complexes $[(\eta^5-C_9H_7)Ru(PPh_3)_2]$ (CH₃CN)]PF₆ ([3]PF₆) [22] and [(η⁵-C₅Me₅)Ru(PPh₃)₂(CH₃CN)] PF_6 ([4] PF_6) [23] were prepared by minor modifications of the literature procedures as described below.

Table 2 Selected bond lengths /Å and angles /° for the complex $([9](PF_6)_2)$

Ru-N(1)	1.9285	Ru-N(22)	2.0884
Ru-P(1)	2.4494(9)	Ru-P(2)	2.4185(9)
Ru-N(32)	2.0717	Ru-N(11)	1.9285
N(1)-C(2)		C(2)-C(3)	1.480(6)
N(22)-Ru-N(11)	78.8	N(11)-Ru-N(32)	79.9
N(22)-Ru-N(1)	100.74(8)	N(32)-Ru-N(1)	100.67(8)
P(1)-Ru-P(2)	174.21(3)		



Figure 3 Molecular structure of the compound $[Ru(PPh_3)_2 (tptz)Cl][PF_6] ($ *[12]PF_6* $) showing with 50 % probable thermal ellipsoids. Hydrogen atoms and PF_6 ion have been omitted for clarity.$

4.1 Preparation of $[(\eta^5 - C_9H_7)Ru(PPh_3)_2(CH_3CN)][PF_6], ([3]PF_6)$

The complex $[(\eta^5-C_9H_7)Ru(PPh_3)_2Cl]$ (1) (100 mg, 0.128 mmol) and NH₄PF₆ (26 mg, 0.24 mmol) were refluxed in 30 ml of acetonitrile for 2 hrs. Within a few minutes, the solution turned yellow and white solid was appeared. The solution was filtered to remove the white solid and the filtrate was rotary evaporated to dryness. 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 (CDCl₃, δ): 2.3 (s, 3H), 4.3 (d, 2H, indenyl), 4.8 (t, 1H, indenyl), 6.9 -7.8 (m, 34H). ³¹P{¹H} NMR (CDCl₃, δ): 54.03 (s, PPh₃); -142 (septet, PF₆⁻, $J_{P-F} =$ 711.39)

4.2 Preparation of $[(\eta^5 - C_5Me_5)Ru(PPh_3)_2(CH_3CN)][PF_6], ([4]PF_6)$

The complex $[Cp*Ru(PPh_3)_2Cl]$ (0.1 g, 0.125 mmol) and NH_4PF_6 (0.041 g, 0.250 mmol) were refluxed in CH₃CN (30 ml) for 2 hrs. During this time the orange red suspension turned yellow and white solid was appeared. The white solid was filtered off and the

Table 3 Selected bond lengths /Å and angles /° of the molecules A and B for the complex $(/12/PF_6)$

	Molecule A	Molecule B
Ru-N(11)	1.812(5)	1.924(5)
Ru-N(31)	2.106(5)	2.145(5)
Ru-P(2)	2.377(6)	2.402(6)
Ru-N(21)	2.166(5)	2.116(5)
Ru-P(1)	2.387(6)	2.440(6)
Ru-Cl	2.434(6)	2.453(6)
N(11)-Ru-N(21)	78.42(19)	77.53(19)
N(11)-Ru-N(31)	77.42(19)	79.36(19)
P(1)-Ru-P(2)	175.2(2)	174.0(2)
P(1)-Ru-Cl	90.1(2)	85.7(2)
P(2)-Ru-Cl	86.7(2)	89.3(2)

filtrate was rotary evaporated. The yellow residue was dissolved in dichloromethane (5 ml) and filtered to remove NH₄Cl and excess NH₄PF₆. The filtrate on concentration to *ca* 5 ml and addition of excess hexane gave yellow crystalline solid. The yellow solid was collected and washed with hexane to afford 83 % yield of the complex.

¹H NMR (CDCl₃, δ): 1.32 (s, 15 H, Cp*), 2.17 (s, 3H, CH₃CN), 6.78 -7.83 (m, 30H).

³¹P{¹H} NMR (CDCl₃, δ): 45.28 (s, PPh₃), -143 (septet, PF₆⁻).

4.3 Preparation of complexes

4.3.1 Preparation of $[(\eta^5 - C_9H_7)Ru(PPh_3)(bpp)][PF_6], ([5]PF_6)]$

The complex $[(\eta^5-C_9H_7)Ru(PPh_3)_2(CH_3CN)]PF_6$, $([3]PF_6)$ (100 mg, 0.107 mmol), the ligand bpp (30 mg, 0.129 mmol) and 40 ml of methanol were mixed in round bottom flask. The resulting mixture was heated to reflux for 4 h. The yellow orange suspension turned into red brown color as the reaction progress. After refluxed for 4 hrs the solution was cooled to room temperature then the solvent was removed under reduced pressure. The brown residue was extracted with dichloromethane and filtered through a short column of silica gel. The filtrate on subsequent concentration to *ca* 5 ml and addition of excess hexane afforded red brown solid. Yield: 75 mg (81 %)

Anal. Calc. for $C_{41}H_{32}N_4P_2F_6Ru$: C, 57.40; H, 3.73; N, 6.53 %. Found: C, 56.78; H, 3.98; N, 6.22 %.

¹H NMR (δ, CDCl₃): 9.64 (d, 1H, $J_{HH} = 3.08$), 9.52 (d, 1H, $J_{HH} = 4.26$), 8.62 (d, 1H, $J_{HH} = 5.83$), 8.34 (d, 1H, $J_{HH} = 3.08$), 7.93 (s, 1H), 7.71 (m, 2H), 7.69 (t, 1H, $J_{HH} = 7.52$), 7.68 (d, 1H, $J_{HH} = 6.92$), 7.55 (d, 1H, $J_{HH} = 2.44$), 6.91-7.51 (m, 17H), 6.56 (d, 2H, $J_{HH} = 3.44$), 4.75 (t, 1H, $J_{HH} = 3.42$), 4.54 (d, 2H, $J_{HH} = 2.84$). -³¹P{¹H} NMR (δ, CDCl₃): 56.68, -140.73 (sept., PF₆, $J_{P-F} = 716$). - UV-vis (λ_{max} , nm): 495.

4.3.2 Preparation of $[(\eta^5 - C_5Me_5)Ru(PPh_3)(bpp)][PF_6], ([6]PF_6)$

This complex was prepared in analogy to $([5]PF_6)$ using the complex $([4]PF_6)$ instead of complex $([3]PF_6)$.

Yield: 76 mg (82 %).

Anal. Calc. for $C_{42}H_{40}N_4P_2F_6Ru$: C, 57.46; H, 4.56; N, 6.38 %. Found: C, 58.32; H, 4.22; N, 5.87 %.

¹H NMR (δ, CDCl₃): 8.90 (d, 1H, $J_{\rm HH}$ = 5.28), 8.61 (d, 1H, $J_{\rm HH}$ = 4.40), 8.57 (t, 1H, $J_{\rm HH}$ = 3.92), 8.47(s, 1H), 8.20 (t, 1H, $J_{\rm HH}$ = 7.60), 7.91-7.12 (m, 20H; 1.33 (s, 15H, Cp*). – ³¹P{¹H} NMR 45.19, -142.71 (sept., PF₆, $J_{\rm P-F}$ = 712). – UV-vis (λ_{max}, nm): 498.

4.3.3 Preparation of $[(\eta^5 - C_9 H_7) Ru(PPh_3)(bpq)][PF_6], ([7]PF_6)]$

The complex was prepared in the same manner as described in $(f5 / PF_6)$ using the ligand bpq (36 mg, 0.129 mmol) instead of bpp. Yield: 77 mg (79 %).

Anal. Calc. for $C_{45}H_{34}N_4P_2F_6Ru$: C, 59.40; H, 3.96; N, 6.16%. Found: C, 58.83; H, 4.12; N, 5.78%.

¹H NMR (δ, CDCl₃): 9.51 (t, 1H, J_{HH} = 3.89), 9.03 (d, 1H, J_{HH} = 8.68), 8.64 (d, 1H, J_{HH} = 4.61), 8.02 (d, 1H, J_{HH} = 8.2), 7.91 (t, 1H, J_{HH} = 5.85), 7.80 (m, 2H), 7.61 (m, 1H), 7.20-7.55 (m, 17H), 6.95 (t, 2H, J_{HH} = 7.83), 6.74 (t, 2H, J_{HH} = 8.13), 6.49 (t, 1H, J_{HH} = 7.08), 6.29 (d, 1H, J_{HH} = 8.63), 5.07 (t, 1H, J_{HH} = 2.74), 4.97 (d, 2H, J_{HH} = 2.16). – ³¹P{¹H} NMR (δ, CDCl₃): 56.25, -143, PF₆, (sept., J_{PF} = 712). – UV-vis (λ_{max} , nm): 490.

4.3.4 Preparation of $[(\eta^5 - C_5 M e_5) Ru(PPh_3)(bpq)][PF_6], ([8]PF_6)$

This complex was prepared in the same manner as described in $([7]PF_6)$ using the complex $([4]PF_6)$ instead of $([3]PF_6)$. Yield: 82 mg, (84 %).

Anal. Calc. for $C_{46}H_{42}N_4P_2F_6Ru$: C, 59.54; H, 4.53; N, 6.04 %. Found: C, 59.23; H, 4.18; N, 5.84 %.

¹H NMR (δ, CDCl₃): 8.67 (d, 1H, $J_{HH} = 5.66$), 8.58 (d, 1H, $J_{HH} = 4.68$), 8.41 (d, 1H, $J_{HH} = 8.36$), 8.07 (t, 2H, $J_{HH} = 4.92$), 7.80 (t, 2H, $J_{HH} = 7.04$), 7.70 (m, 1H), 7.55 (t, 1H, $J_{HH} = 8.16$), 7.48-6.88 (m, 18H), 1.37 (s, 15H, Cp*). – ³¹P{¹H} NMR (δ, CDCl₃): 44.76, -142.83, PF₆, ($J_{P-F} = 712$). – UV-vis (λ_{max} , nm): 510.

4.3.5 Preparation of $[Ru(PPh_3)_2(tppz)CH_3CN)][PF_6]_2$, $([9](PF_6)_2)$

round bottom flask was charged with [(n⁵-A C_9H_7)Ru(PPh₃)₂(CH₃CN)]PF₆, (/3/PF₆) (100 mg, 0.107 mmol), tppz (0.202 mmol) and methanol (40 ml). The mixture was then heated to reflux for 5 h under nitrogen atmosphere. The color of the solution progressively changed from yellow orange to dark brown as the reaction proceeded. The solution was cooled to room temperature, and then the solvent was removed by rotary evaporator. The residue was extracted with dichloromethane and poured onto silica gel column. A dark brown color band collected using dichloromethane/acetone mixture 1:5 (v/v) as an eluent. The solution was concentrated to ca. 5 ml and excess of hexane was added whereby the compound precipitated out as dark brown solid. The solid was washed with hexane 2x20 ml and dried under vacuum. Yield: 84 mg (58 %).

Anal. Calc. for $C_{62}H_{49}F_{12}N_7P_4Ru$: C, 55.31; H, 3.64; N, 7.28 %. Found: C, 54.93; H, 3.86; N, 6.78 %.

¹**H** NMR (δ , CDCl₃): 9.28 (d, 1H, $J_{HH} = 8.24$), 8.95 (d, 1H, $J_{HH} = 7.36$), 8.69 (d, 1H, $J_{HH} = 3.21$), 8.66 (d, 1H, $J_{HH} = 5.26$), 8.59 (d, 1H, $J_{HH} = 5.34$), 8.42 (d, 1H, $J_{HH} = 3.86$), 8.36 (d, 1H, $J_{HH} = 7.56$), 8.28 (d, 1H, $J_{HH} = 6.24$), 8.08 (t, 2H, 7.64), 8.02 (t, 2H, $J_{HH} = 5.34$), 7.96 (m, 2H), 7.78-6.73 (m, 28H), 6.75 (d, 1H, $J_{HH} = 3.66$), 6.73 (t, 1H, $J_{HH} = 4.8$), 6.57 (m, 1H), $J_{eH} = 10.82$), 2.75 (s, 3H). – ³¹P{H} NMR (δ , CDCl₃): 24.98, –140.19, PF₆, (sept., $J_{P-F} = 712$). – UV-vis (λ_{max} , nm): 435, 375, 345, 318.

4.3.6 Preparation of $[Ru(PPh_3)_2(tppz)Cl][PF_6]$, $([10]PF_6)$

The compound $[(\eta^5-C_9H_7)Ru(PPh_3)_2(CH_3CN)]PF_6$, $(f3]PF_6)$ (100 mg, 0.107 mmol) was initially dissolved in minimum amount of dichloromethane and 40 ml of toluene was added. To this solution tppz (49 mg, 0.126 mmol) was added and the resulting mixture was heated to reflux under nitrogen atmosphere for 5h. The reaction mixture was cooled to room temperature and the solvent was removed under reduce pressure. The residue was extracted with dichloromethane and chromatograph on silica gel column. A light brown band was collected using dichloromethane: acetone mixture (2:5 v/v) as eluent. A comparatively less amount of second band collected by using methanol, as eluent was not characterized.

Yield: 72 mg (56 %). Analytical Calc. for: $C_{60}H_{46}F_6N_6P_3Ru$: C, 60.32; H, 3.85; N, 7.03 %.

Found: C, 59.27; H, 3.15; N, 6.82 %.

¹**H** NMR (δ , CDCl₃): 9.46 (d, 1H, $J_{\rm HH}$ = 4.8), 9.10 (d, 1H, $J_{\rm HH}$ = 15.32), 8.95 (d, 1H, $J_{\rm HH}$ = 5.08), 8.66 (d, 1H, $J_{\rm HH}$ = 4.24), 8.04 (t, 1H, $J_{\rm HH}$ = 1.76), 7.77 (d, 1H, $J_{\rm HH}$ = 7.72), 7.67 (d, 1H, $J_{\rm HH}$ = 8.32), 7.64 (d, 1H,

 $J_{\rm HH}$ = 6.96), 7.57 (t, 2H, $J_{\rm HH}$ = 6.74), 7.53 (t, 2H, $J_{\rm HH}$ = 7.52), 7.40 (m, 2H), 7.31(m, 2H), 7.29-6.74 (m, 28H), 6.22 (d, 2H, $J_{\rm HH}$ = 7.88). – ³¹P{¹H} NMR (δ , CDCl₃): 24.98, –142, (sept., PF₆, $J_{\rm P-F}$ = 712). – UV-vis ($\lambda_{\rm max}$, nm): 430, 370, 354, 315.

4.3.7 $[Ru(PPh_3)_2(tptz)CH_3CN)][PF_6]_2$, $([11](PF_6)_2)$

This compound was prepared in analogy to that of compound $([9](PF_6)_2)$ using the ligand tptz instead of tppz. The compound was obtained by column chromatography on silica gel column collecting the red band using dichloromethane: acetone (2:6, v/v) as eluent, the second purple band eluted with methanol was not characterized.

Yield: 79 mg (58 %). Analytical Calc. for: $C_{56}H_{45}F_{12}N_7P_4Ru:$ C, 52.96; H, 3.54; N, 7.72 %.

Found: C, 53.28; H, 3.17, N, 7.34 %.

¹H NMR (δ, CDCl₃): 9.82 (d, 2H, $J_{\rm HH}$ = 5.7), 9.54 (d, 2H, $J_{\rm HH}$ = 4.2), 9.13 (d, 1H, $J_{\rm HH}$ = 5.5), 9.01(d, 2H, $J_{\rm HH}$ = 3.9), 8.94(m, 2H), 8.84 (m, 2H), 8.73(d, 1H, $J_{\rm HH}$ = 7.8), 8.55(d, 1H, $J_{\rm HH}$ = 11.6), 8.22 (d, 1H, $J_{\rm HH}$ = 8.9), 8.17-6.99 (m, 26H), 6.91 (d, 2H, $J_{\rm HH}$ = 6.2), 2.79 (s, 3H, CH₃CN). ³¹P{¹H} NMR (δ, CDCl₃): 28.62, -144.40 (sept., PF₆, $J_{\rm P-F}$ = 713). – UV-vis ($\lambda_{\rm max}$, nm): 495, 354, 318.

4.3.8 $[Ru(PPh_3)_2(tptz)Cl)][PF_6], ([12]PF_6)$

This complex was prepared by following a procedure as $([10]PF_6)$ using the ligand tptz instead of tppz. Following a work up as $([10]PF_6)$, a brown color compound was collected using dichloromethane: acetone 2:5(v/v) as eluent. A comparatively less quantity of purple color compound was isolated as the second band by using methanol, as eluent was not characterized.

Yield: 74 mg (62 %). Analytical Calc. for: $C_{54}H_{42}ClF_6N_6P_3Ru$: 57.94; H, 3.75; N, 7.51

Found: C, 57.28; H, 3.96; N, 7.24 %.

¹H NMR (δ, CDCl₃): 9.15 (d, 2H, $J_{\rm HH}$ = 5.3), 8.94 (d, 2H, $J_{\rm HH}$ = 4.3), 8.80 (d, 1H, $J_{\rm HH}$ = 5.2), 8.58 (d, 2H, $J_{\rm HH}$ = 7.2), 8.16 (m, 1H), 7.98(d, 1H, $J_{\rm HH}$ = 7.3), 7.94 (t, 2H, $J_{\rm HH}$ = 7.3), 7.62 (m, 2H), 7.41(d, 2H, $J_{\rm HH}$ = 5.8), 7.39-6.93 (m, 27H). – ³¹P{¹H} NMR (δ, CDCl₃): 13.80, -142 (sept., PF₆, $J_{\rm P-F}$ = 711). – UV-vis ($\lambda_{\rm max}$, nm): 480, 328, 315.

4.4 Structure analysis and refinement:

X-ray quality crystals of complexes $(/9/(PF_6)_2)$ and $(/12/PF_6)$ were grown by slow diffusion of hexane in dichloromethane solution of $(/9/(PF_6)_2)$ and $(/12/PF_6)$. The X-ray intensity data were measured at 293(2) K for complex $([9](PF_6)_2)$ and 183(2) K for complex $(/12/PF_6)$ on a Bruker Smart Apex CCD area detector employing graphite monochromater using M₀-K α radiation (λ = 0.71073 Å). Intensity data were corrected for Lorentz and polarization effects and absorption correction was made using SAINT program [24]. An empirical absorption correction was made by modeling a transmission surface by spherical harmonics employing equivalent reflections with I> $2\sigma(I)$ (program SADBAS) [25]. The structures were solved by direct methods [26] and refined by full matrix least squares base on F² using SHELXL-97 software [27]. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a "riding" model. Refinement converged at a final R = 0.0496 and 0.0857 (for complex $(/9/(PF_6)_2)$) and $(/12/PF_6)$ respectively, for observed data F), and wR₂ = 0.1300 and 0.2096 (for complex $(/9/(PF_6)_2)$ and $(/12/PF_6)$ respectively, for unique data F²).

5 Concluding Remarks

Four new mononuclear indenyl and pentamethylcyclopentadienyl ruthenium complexes and four coordination complexes of some polypyridyl ligands have been prepared and fully characterized. The study highlight the more labile nature of indenvl ligand as compared to analogous cyclopentadienyl ligand that indenyl ligand is readily substituted by sterically demanding tridentate N- base ligands such tppz or tptz whereas under similar condition Cp ligand does not. Further, with less steric N base ligand such as bpp or bpq the indenvl group remains intact to the metal and forming corresponding nitrogen chelated indenyl ruthenium complexes. It can be concluded that reaction of complex $(/3/PF_6)$ with less steric ligand does not displaced the indenyl group while with sterically demanding ligand displaced indenyl group from the complex. Thus, the stabilty of indenyl ligand is largely depend on the steric nature of the incoming ligand, sterically demanding N-base ligand displaced it from the complexes while less sterically demanding ligand, resulted N-chelated indenvl complexes.

Supplementary material: Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre (CCDC), CCDC No. 268654 for complex $([9](PF_6)_2)$ and CCDC No. 268655 for complex $([12]PF_6)$. 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).

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