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Syntheses and characterization of indenylruthenium(II) complexes containing N,N' donor Schiff base ligands. Molecular structures of $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2(CH_3CN)]BF_4$ and $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(C_5H_4\text{–}N\text{-}2\text{–}CH{=}N\text{–}C_6H_4\text{-}p\text{-}CH_3)]BF_4$ ☆

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Abstract

Reaction of the complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ (**1**) with acetonitrile in the presence of NH_4BF_4 leads to formation of the complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2(CH_3CN)]BF_4$ (**2**). The complex (**2**) undergoes reactions with a series of N,N' donor Schiff bases, viz., *para*-substituted N-(pyrid-2-ylmethylene)-phenylamines (ppa) in methanol yielding indenyl ruthenium(II) Schiff base complexes of formulation $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(C_5H_4N\text{-}2\text{–}CH{=}N\text{–}C_6H_4\text{-}p\text{-}X)]BF_4$ (**3a**–**3e**), where C_9H_7 = indenyl, X = H (**3a**), Me (**3b**), OMe (**3c**), NO_2 (**3d**), and Cl (**3e**), respectively. These complexes were fully characterized on the basis of elemental analyses and NMR spectroscopy. The molecular structures of the starting complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2(CH_3CN)]BF_4$ (**2**) and a representative complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(C_5H_4N\text{–}CH{=}N\text{–}C_6H_4\text{-}p\text{-}CH_3)]BF_4$ (**3b**) have been established by X-ray diffraction study.

Keywords: Ruthenium; Indenyl; Schiff bases; Pyridine-2-carboxaldehyde

1. Introduction

The chemistry of cyclopentadienyl and indenyl ruthenium bisphosphine complexes, viz., $[CpRu(PPh_3)_2Cl]$ and $[(ind)Ru(PPh_3)_2Cl]$ (**1**), has generated a lot of interest during the past few decades due to their high reactivity [1] and catalytic activity [2]. Their chemistry is characterized by the ready displacement of one of the triphenylphosphine ligand and a chloride ligand by the incoming ligands. The steric interaction of the two triphenylphosphines often leads to the ready displacement of one of them by other ligands during the course of the reaction. Most of the reactions of these complexes center on displacement of one or both triphenylphosphine units or one of the triphenylphosphine units along with chloride to yield neutral or cationic complexes [3–5]. There has been an extensive study on the chemistry of cyclopentadienyl ruthenium(II) $[CpRu(PPh_3)_2Cl]$ with a variety of ligands [6]. However, the analogous indenyl ruthenium bisphosphine complexes have not been much explored due to the lack of good synthetic procedures and convenient precursor complexes. The complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ differs from the analogue $[CpRu(PPh_3)_2Cl]$ in certain aspects such as higher reactivity and lability of the indenyl ligand. Their higher reactivity is attributed to the ring slippage from η^5 to η^3 and back to η^5 of the indenyl ligand [7]. Reaction of the complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ with N-donor bases in methanol yielded the complexes without the indenyl

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group resulting in simple coordination compounds [8]. In contrast, its analogous complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ under similar conditions yielded N-coordinated complexes of the type $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)L_2]^+$ [9] where L_2 = 4-phenyl-2,2′:6,2″-terpyridine, 2,3-bis(α-pyridyl)quinoxaline, tetra-2-pyridyl-1,4-pyrazine, etc. Recently, some reports have appeared on the reactivity of indenyl ruthenium complexes with a variety of alkynols [10]. However, insofar as our knowledge goes, the chemistry of bidentate nitrogen chelating indenyl ruthenium(II) phosphine complexes of the type $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(L_2)]^+$ (where L_2 = *N*-donor bidentate or tridentate ligands) remains relatively unexplored. The high reactivity of these complexes and labile nature of indenyl ligand has prompted us to study their chemistry. Although there exists an extensive work on the chemistry of monocyclopentadienyl transition metal [11] and arene ruthenium [12a] Schiff base complexes, the chemistry of the corresponding indenyl complexes has not been studied prior to the commencement of this work. In this present work, we describe the synthesis of indenyl ruthenium(II) complexes of Schiff base ligands using the precursor complex (**2**). As a part of our investigation on their chemistry, we report herein the syntheses of new cationic indenyl ruthenium(II) phosphine complexes of *N*′,*N*-donor Schiff base ligands (**3a**–**3e**).

2. Experimental

2.1. General remarks

All reactions were carried out in distilled and dried solvents under nitrogen atmosphere. $RuCl_3 \cdot 3H_2O$ 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. Elemental analyses (C, H, N) were performed using a Perkin–Elmer-2400 CHNS/O analyzer. FT IR spectra were recorded on a Perkin–Elmer-model 983 spectrophotometer with the sample prepared as KBr pellets. Electronic spectra were recorded on a Hitachi-330 spectrophotometer. Conductivity measurements were made on a Wayne Kerr automatic precession bridge B905 using ca. 10^{-4} M solution in dry acetonitrile at room temperature (Λ_m values are given in S cm^2 mol^{-1}). The ^{1}H NMR spectra were recorded in $CDCl_3$ solvent with tetramethylsilane as internal standard and recorded on a Bruker ACF-400 MHz spectrometer; coupling constants *J* were given in hertz. $^{31}P\{^1H\}$ NMR chemical shifts were recorded relative to H_3PO_4 (85%). The ligands C_5H_4N-2-CH=C_6H_4-*p*-X (where X = H, Me, OMe, Cl, NO_2), [13] and the precursor complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ [14] were prepared following methods quoted in the literature.

2.2. Syntheses of precursor complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2(CH_3CN)]BF_4$ (2)

This complex was prepared by a slight modification of the reported method [14] as delineated here. The complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ (**1**) (100 mg, 0.128 mmol) and NH_4BF_4 (268 mg, 0.256 mmol) were refluxed in 30 ml of acetonitrile for 2 h. Within a few minutes, the solution turned yellow and a white solid appeared. The solution was filtered to remove the white solid and the filtrate was rotary-evaporated. The residue was extracted with 5 ml of dichloromethane and filtered into 50 ml of hexane, whereby the product precipitated out as a yellow crystalline solid.

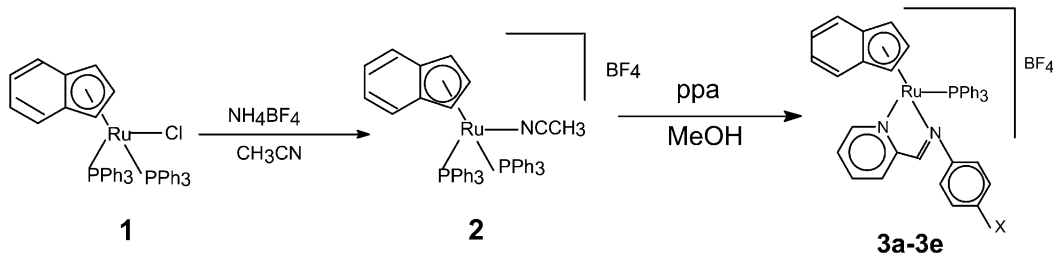
^{1}H NMR ($CDCl_3$, δ): 2.3 (s, 3H), 3.9 (d, 2H, indenyl), 4.3 (t, 1H, indenyl), 6.9–7.8 (m, 34H, arene ring of indenyl and triphenylphosphines).

2.3. Syntheses of $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(C_5H_4N\text{-}2\text{–}CH{=}N\text{–}C_6H_4\text{-}p\text{-}X)]BF_4$ (3) complexes [X = H (3a), Me (3b), OMe (3c), NO_2 (3d), Cl (3e)]

These complexes were prepared using a general method in which the acetonitrile complex (**2**) (100 mg, 0.115 mmol) and the appropriate ligand (0.230 mmol) were refluxed in 20 ml of methanol. The yellow solution turned into a dark brown solution within few minutes and the resulting solution was refluxed for a further 1.5 h under nitrogen atmosphere. The solvent was removed in a rotary evaporator to dryness and the residue was dissolved in chloroform and filtered through a short silica gel column. The filtrate on subsequent concentration and addition of excess diethyl ether gave the complexes **3a**–**3e** as a dark brown solid. The solid was washed with hexane (2 × 10 ml) and finally with diethyl ether, then dried under vacuum to afford a 75–83% yield of the complexes.

3. Structure analysis and refinement

X-ray quality crystals of the complex **2** were grown by slow diffusion of hexane in a dichloromethane solution of **2**, while the crystals of **3b** were grown in the same manner using hexane and acetone. The X-ray intensity data were measured at 293(2) K for complex **2** and at 143 K for complex **3b** on a Rigaku Mercury CCD area detector employing graphite monochromater using Mo Kα radiation ($\lambda = 0.71069$ Å). Intensity data were corrected for Lorentz and polarization effects, absorption corrections being made using REQAB [15]. The structures were solved by direct methods (SIR 97) [16] and refined by a full-matrix least squares method on F^2 using the SHELXL-97 software [17]. The weighing scheme used was $W = 1/[\sigma^2(F_o^2) + 0.0311P^2 + 3.5016P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined aniso-



1 2 3a-3e

ppa= N-(pyrid-2-ylmethylene)phenylamine

Scheme 1.

tropically and hydrogen atoms were refined using a "riding" model. Refinement converged at a final value of $R = 0.0535$ and 0.0346 for complexes **2** and **3b**, respectively (for observed data F), and at values of $wR_2 = 0.1386$ and 0.0782 for complexes **2** and **3b**, respectively (for unique data F^2).

4. Results and discussion

The starting acetonitrile complex $[(\eta^5\text{-}C_9H_7)\text{-}Ru(PPh_3)_2(CH_3CN)]BF_4$ (**2**) was prepared by refluxing the complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ with acetonitrile in the presence of NH_4BF_4. The reaction of complex (**2**) with two equivalents of ppa ligand in methanol gave brown colored and air stable cationic complexes **3a**–**3e** (Scheme 1).

The reaction of complex **1** with Schiff base ligands in polar solvents did not give the desired complexes even after refluxing for a long period of time. However, when the reaction was carried out using its acetonitrile complex (**2**), the complexes **3a**–**3e** were formed in good yield, which indicates that the complex (**2**) is a better precursor than (**1**) for the syntheses of N,N-donor bases

Table 1
Analytical[a], FT IR, ^{1}H NMR[b] and ^{31}P NMR of the complexes **3a**–**3e**

Complex	Analyses (%)			IR (KBr Pellets, cm^{-1})	^{1}H NMR [multiplicity, nH, J (Hz)]	^{31}P NMR (δ)
	C	H	N			
3a	62.1	4.5	3.9	1592 ($\nu_{C=N}$)	9.47 (d, 1H, 5.4), 8.61 (s, 1H), 8.33–7.12 (m, 25H) 6.75 (d, 2H) 5.36 (t, 1H, indenyl); 4.57 (d, 2H, indenyl)	55.13
	(62.6)	(4.3)	(3.7)	1082 (ν_{B-F})		
3b	62.8	4.3	3.4	1589 ($\nu_{C=N}$)	9.51 (d, 1H, 5.2), 8.59 (s, 1H); 8.13–6.94 (m, 24H); 6.71 (d, 2H) 5.41 (t, 1H, indenyl); 4.54 (d, 2H, indenyl); 2.39 (s, 3H)	55.32
	(63.1)	(4.5)	(3.6)	1089 (ν_{B-F})		
3c	61.1	4.6	4.2	1598 ($\nu_{C=N}$)	9.43 (d, 1H, 5.4); 8.42 (s, 1H); 8.34–7.21 (m, 24H); 6.94 (d, 2H) 5.36 (t, 1H, indenyl); 4.58 (d, 2H, indenyl); 3.86 (s, 3H)	55.27
	(61.7)	(4.4)	(3.7)	1089 (ν_{B-F})		
3d	58.8	4.2	5.8	1593 ($\nu_{C=N}$)	9.42 (d, 1H, 5.4); 8.32 (s, 1H); 8.14–6.92 (m, 24H); 6.88 (d, 2H) 5.34 (t, 1H, indenyl); 4.58 (d, 2H, indenyl)	54.44
	(59.1)	(3.9)	(5.2)	1089 (ν_{B-F})		
3e	59.1	3.8	3.5	1598 ($\nu_{C=N}$)	9.46 (d, 1H, 5.6); 8.76 (s, 1H); 8.42–6.96 (m, 24H); 6.72 (d, 2H) 5.37 (t, 1H, indenyl); 4.55 (d, 2H, indenyl)	54.56
	(59.9)	(4.9)	(3.6)	1083 (ν_{B-F})		

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

Table 2
UV–Visible and conductivity data of the complexes at room temperature

Complexes	λ max (nm)	Conductivity Λ_m (S cm^2 mol^{-1})
$[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(C_5H_4N\text{-}2\text{–}CH{=}N\text{–}C_6H_5)]BF_4$	465	180
$[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(C_5H_4N\text{-}2\text{–}CH{=}N\text{–}C_6H_4\text{-}p\text{-}CH_3)]BF_4$	468	172
$[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(C_5H_4N\text{-}2\text{–}CH{=}N\text{–}C_6H_4\text{-}p\text{-}OCH_3)]BF_4$	470	159
$[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(C_5H_4N\text{-}2\text{–}CH{=}N\text{–}C_6H_4\text{-}p\text{-}NO_2)]BF_4$	445	167
$[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(C_5H_4N\text{-}2\text{–}CH{=}N\text{–}C_6H_4\text{-}p\text{-}Cl)]BF_4$	454	145

containing indenyl ruthenium phosphine complexes. These complexes can also be prepared by refluxing the complex (**2**) with the appropriate ligands in a dichloromethane/benzene 1:10 mixture for 3–4 h. The complexes are highly soluble in polar solvents such as dichloromethane, acetone, etc., but insoluble in non-polar solvents such as hexane, pentane, etc., C, H, N analyses, IR, ^{1}H, and ^{31}P NMR spectroscopic data (Table 1) supported the formation of these complexes (**3a**–**3e**). The X-ray structures of the starting complex (**2**) and a representative complex **3b** were determined to confirm the structure of the complexes. The IR spectra of all these complexes show strong bands due to the phenyl groups of triphenylphosphine. The $\nu_{C=N}$ group of the ligands absorbed at around 1590 cm^{-1} while the BF_4 group exhibited a strong band for ν_{B-F} in the range 1082–1089 cm^{-1}. The proton NMR spectra of these complexes (**3a**–**3e**) exhibited a doublet at around δ 4.5 (H20 and H22) and a triplet at δ 5.3 (H21) for the cyclopentadienyl ring protons of the indenyl group, indicating a downfield shift from the starting complex (**2**). However, in the complex (**2**) these protons were observed at δ 3.9 and δ 4.3, respectively. The resonance of the *ortho* proton of the pyridine ring of the ligand is observed as a doublet in the range δ 9.5–9.2 in these complexes. A singlet observed at around δ 8.58 could be due to the methine proton of the pyridylimine group. The proton NMR spectra of all these complexes show a multiplet in the range of δ 8.42–6.92 due to the phenyl protons of the triphenylphosphine moiety, the arene ring of the indenyl group, the N-heterocyclic ring and amine group of the ligands (ppa). The ^{31}P spectra of these complexes exhibited sharp resonance in the range of δ 54.44–55.32 due to the triphenylphosphine moiety as compared to δ 46.5 observed in the neutral complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ [14]. This downfield chemical shift indicates the cationic nature of these complexes following substitution of one chloride ion and one triphenylphosphine unit by the ligands. The electronic spectra and conductivity data of these complexes are shown in Table 2. The electronic spectra of these complexes in dichloromethane exhibited absorption bands in the range of 445–470 nm. This low energy absorption is assigned to the metal-ligand ($d\pi - \pi^*$) charge transfer (MLTC) transition (from the ruthenium filled *4d*-orbital to the ligand empty π^* orbital). The molar conductivity of the complexes in acetonitrile ranges from 145 to 180 S cm^2 mol^{-1}, thereby suggesting that these complexes are ionically dissociated in 1:1 ratio [18].

5. Crystal structures

The structure of the complexes **2** and **3b** consists of complex cations and BF_4 anions joined by columbic forces. The perspective views of each complex including the atom numbering schemes are shown in Figs. 1 and 2.

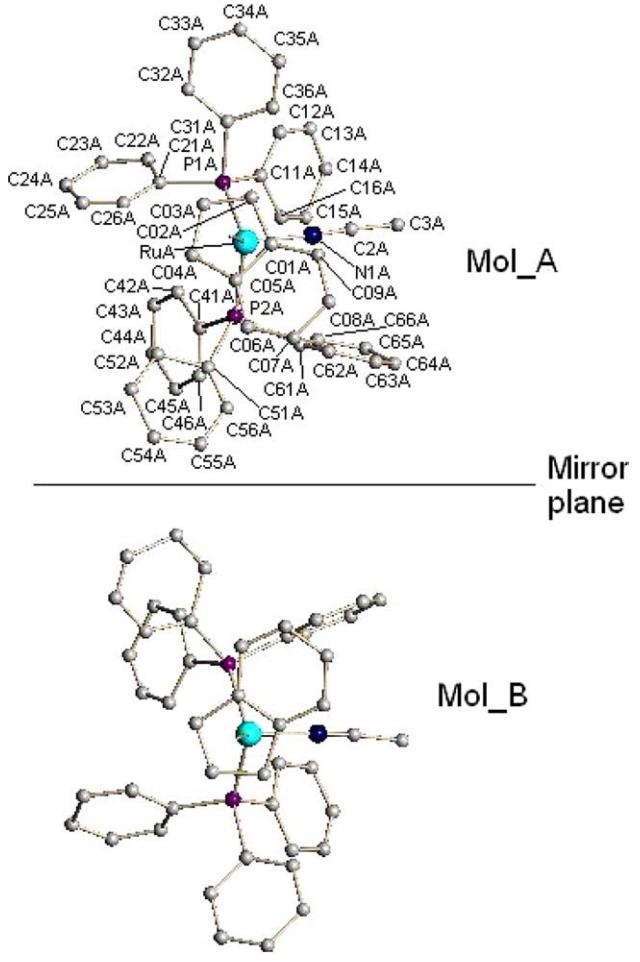


Fig. 1. Molecular structure of complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2(CH_3CN)]BF_4$ (**2**) (molecule **A**) with labeling scheme. Hydrogen atoms have been omitted for clarity.

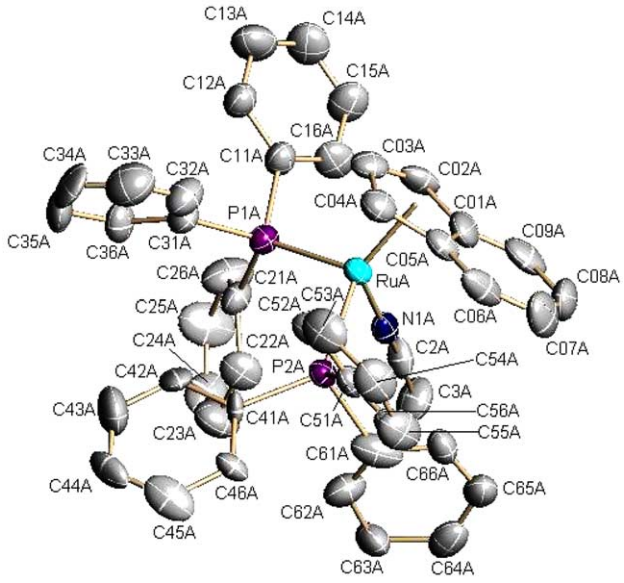


Fig. 1 (*continued*).

Details of the crystallographic data collection are summarized in Table 3. Selected bond lengths and angles are listed in Tables 4 and 5.

The complex **2** crystallizes in the space group $P2_1$. The ruthenium atom is hexa-coordinated with three facial coordination sites occupied by the indenyl ligand, two sites by the P atoms of the two triphenylphosphines, and the remaining one by the N atom of the acetonitrile ligand. The ruthenium atom is π-bonded to the indenyl ligand with the distance between ruthenium and the centroid of the five membered indenyl ring equal to 1.879 Å. The indenyl group is bonded to the metal in pentahapto fashion and displays the asymmetric coordination of the metal and carbon atom of the five-membered ring. The three Ru–C bond lengths in both enantiomorphs involving the C(01), C(02), C(03) atoms are significantly shorter than those involving bridging C(04) and C(05) atoms (Table 4) as found in other indenyl complexes [7,10a]. The asymmetric metal-carbon bond distance is due to the slipping of ruthenium across the η^5- to η^3-coordination [19]. Although the indenyl group is η^5-bonded to the metal atom, the structure shows slight distortion of the five-membered ring from complete planarity. A similar feature of asymmetric Ru–C bond distances is also observed in the complex **3b** (Table 5). An interesting nature of the crystal is that it shows enantiomorphism. The enantiomorphs are assigned as molecule A and molecule B in the ORTEP diagram (Fig. 1). They are identical in structure and cannot be superimposed through rotation in space, having no S_n axis of symmetry. The enantiomorphism is due to the restricted rotation of the C_9H_7 unit in the crystal, which is spatially fixed with respect to the other parts of the molecule. However, in solution the molecules are indistinguishable due to the free rotation of the C_9H_7 unit around the ruthenium atom and do not give distinct molecules. The distance between the ruthenium atom and the centroid of the ring in molecule A (1.879 Å) and molecule B (1.893 Å) falls within the range found in other indenyl ruthenium complexes [10a]. The Ru–N bond length in both the enantiomorphs (2.015(8) Å for molecule A, and 2.059(8) Å for molecule B) is comparable to that of Ru–N bond lengths of other

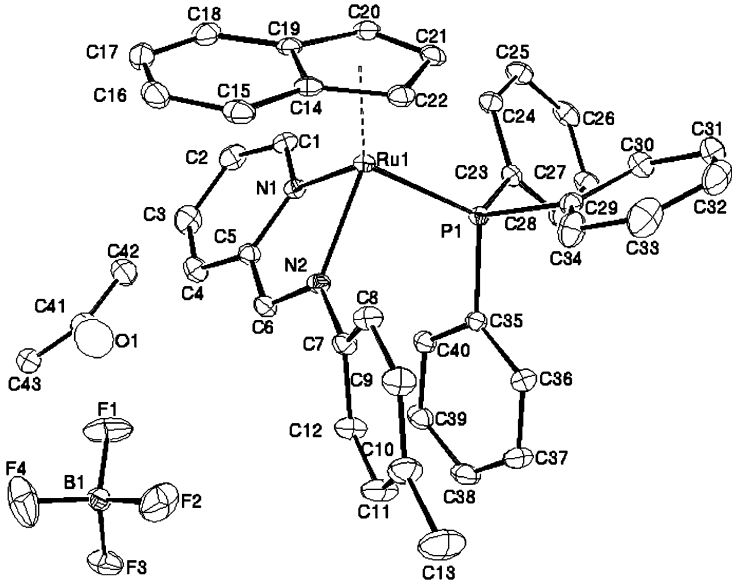


Fig. 2. Molecular structure of complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(C_5H_4N\text{–}CH{=}N\text{–}C_6H_4\text{-}p\text{-}CH_3)]BF_4$ (**3b**) with 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Table 3
Summary of structure determination of complex **2** and complex **3b** acetone

Empirical formula	$C_{47}H_{40}BF_4NP_2Ru$	$C_{43}BH_{40}N_2POF_4Ru$
Formula weight	868.62	819.62
Temperature (K)	293(2)	143
Wavelength (Å)	0.71073	0.71069
Crystal system	Monoclinic	Monoclinic
Space group	P_1	$P2_1/n$ (#14)
Unit cell dimensions		
a (Å)	13.1595(8)	10.8709(5)
b (Å)	15.498(1)	16.7639(7)
c (Å)	19.823(1)	20.7207(9)
β (°)	96.917(1)	92.2891(4)
Volume (Å^3)	4013.5(4)	3773.1(3)
Z	4	4
Density (calculated)	1.438 Mg/m^3	1.443 g/cm^3
Absorption coefficient	0.524 mm^{-1}	5.15 cm^{-1}
$F(000)$	1776	1680
Crystal size (mm)	$0.3 \times 0.4 \times 0.6$	$0.38 \times 0.26 \times 0.20$
θ range for data collection	1.03° to 28.30°	2θ range 5.24–54.96°
Index ranges	$-16 \leqslant h \leqslant 17$; $-20 \leqslant k \leqslant 19$; $-26 \leqslant l \leqslant 25$	$-10 \leqslant h \leqslant 13$; $-18 \leqslant k \leqslant 21$; $-26 \leqslant l \leqslant 24$
Reflections collected	34326	23284
Independent reflections (R_{int})	17787 (0.0215)	8440 (0.0205)
Number of observed reflections		7341 ($F > 4\sigma$)
Absorption correction	Empirical (SADABS)	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	17787/1/796	8440/1/481
Goodness-of-fit on F^2	1.013	1.097
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0535$, $wR_2 = 0.1386$	($F > 4\sigma$] $R_1 = 0.0346, wR_2 = 0.0782$
R indices (all data)	$R_1 = 0.0765$, $wR_2 = 0.1595$	$R_1 = 0.0420$, $wR_2 = 0.0845$
Largest differential peak and hole (e Å^{-3})	1.664 and −1.202	+1.095 and −0.560

Table 4
Selected bond distances (Å) and bond angles (°) of the enantiomorphs molecule A and molecule B of the complex **2**

	Molecule A	Molecule B
Bond lengths		
Ru–N(1)	2.015(8)	2.059(8)
C*–Ru	1.879	1.893
Ru–C(01)	2.254(5)	2.342(5)
Ru–C(02)	2.165(8)	2.192(10)
Ru–C(03)	2.160(9)	2.175(10)
Ru–C(04)	2.206(10)	2.204(8)
Ru–C(05)	2.366(5)	2.321(5)
Ru–P(1)	2.300(2)	2.397(2)
Ru–P(2)	2.389(2)	2.300(2)
N(1)–C(02)	1.161(12)	1.095(12)
Bond angles		
N(1)–Ru–P(1)	86.12(19)	89.5(2)
P(1)–Ru–P(2)	104.65(7)	104.52(8)
N(1)–Ru–P(2)	90.0(2)	86.6(2)
C(01)–Ru–N(1)	93.8(2)	117.1(2)
C(02)–Ru–N(1)	100.6(4)	153.5(3)
C(03)–Ru–N(1)	135.0(3)	135.9(4)
C(04)–Ru–N(1)	153.8(3)	99.1(3)
C(05)–Ru–N(1)	118.4(2)	91.4(2)

C* = Centroid of C(01), C(02), C(03), C(04), C(05).

related complexes [20]. The Ru–P(1) and Ru–P(2) bond lengths are 2.300 and 2.389 Å, respectively, which are within the range observed in reported complexes.

Table 5
Selected bond lengths (Å) and bond angles (°) of complex **3b**

Bond lengths			
Ru–N(1)	2.089(2)	Ru–P(1)	2.2715(6)
Ru–N(2)	2.122(2)	N(2)–C(6)	1.297(3)
C**–Ru	1.8648(2)	Ru–C(20)	2.178(2)
Ru–C(14)	2.322(2)	Ru–C(21)	2.161(2)
Ru–C(19)	2.303(2)	Ru–C(22)	2.200(2)
Bond angles			
N(1)–Ru–N(2)	76.44(7)	C(19)–Ru–P(1)	148.08(6)
N(1)–Ru–P(1)	96.12(5)	C(20)–Ru–P(1)	110.64(6)
N(2)–Ru–P(1)	90.61(5)	C(21)–Ru–P(1)	90.17(6)
C(14)–Ru–P(1)	143.12(6)	C(22)–Ru–P(1)	106.01(6)

C** = Centroid of C(14), C(19), C(20), C(21), C(22).

The complex **3b** crystallizes in the $P2_1/n$ space group. The crystal structure consists of a mononuclear cationic unit $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(C_5H_4\text{–N-2–CH=N–}C_6H_4\text{-}p\text{-}CH_3)]^+$, the tetrafluoroborate anion and one acetone molecule per complex molecule. The ruthenium atom is π-bonded to the cyclopentadienyl ring of the indenyl ligand with an average Ru–C distance of 2.2328 Å, whereas the distance between the ruthenium atom and the centroid of the ring is 1.8648(2) Å. In addition to being bonded to one indenyl and one triphenylphosphine ligand, the ruthenium atom is also directly coordinated to two nitrogen atoms of the ligand with an average distance of 2.1055(2) Å. The bite

angle of the chelating ligand N(1)–Ru(1)–N(2) is 76.44(7)° which is very close to that observed in the related complexes [8a]. The phenyl ring of the amine is slightly twisted out of the plane of the pyridine ring in contrast to the observed mutually perpendicular orientation found with similar types of ligand in arene ruthenium complexes [21].

The indenyl group in the complex is bonded to the ruthenium atom in η^5-fashion and displays the asymmetric coordination generally observed with this ligand [19]. Thus, the Ru–C(20), Ru–C(21), Ru–C(22) bond lengths (2.178(2), 2.161(2) and 2.200(2) Å, respectively) are shorter than for those between ruthenium and bridging carbon atoms (where the Ru–C(14) and Ru–C(19) bond lengths are 2.322(2) and 2.303(2) Å, respectively). The asymmetry is explained on the basis of slippage from η^5-bonded coordination to η^3-coordination. The five-membered ring here is not a regular pentagon, as observed in other indenyl complexes [22]. There is no significant difference in the five C–C bond lengths in the five-membered ring, the bond lengths falling within the range of 1.411(3)–1.449(3) Å, which suggests delocalization of the double bonds in the ring. The benzene ring is planar and does show significant localization of the double bonds at the C(15)–C(16) bond (1.367 Å) and the C(17)–C(18) bond (1.369(4) Å) as previously found for other indenyl complexes [19]. Both these bond lengths are significantly shorter than those for the C(14)–C(15) bond (1.417(3) Å), the C(16)–C(17) bond (1.410(3) Å) and the C(18)–C(19) bond (1.420(3) Å). The Ru(1)–P(1) bond length is 2.2715(6) Å, which is within the usual range of Ru–P bond distances (2.20–2.43 Å) [23]. The geometry of the complex is octahedral with the cyclopentadienyl moiety of the indenyl ligand occupying three coordination sites. This is evident by the nearly 90° values for the bond angle N(1)–Ru–P(1) between the non-indenyl ligands (96.12(5)°) and for the bond angle N(2)–Ru–P(1) (90.61(5)°) at the metal centre. Overall there are no significant differences between the complex **3b** and the complex **2** in the indenyl C–C bond lengths and the distance between ruthenium and the centroid of the ring.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre (CCDC) at CCDC No. 224681 for complex **2** and CCDC No. 224682 for complex **3b**. 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; email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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