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Synthesis and characterization of $[(Cp^*)Ru(PPh_3)(N\text{-base})]X$ and $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(N\text{-base})]X$ complexes: crystal and molecular structure of the complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(phen)]PF_6$ ($Cp^* = C_5Me_5$, indenyl $= C_9H_7$; N-bases = bipy. and phen.; $X = BF_4$ or PF_6)

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Abstract

The reactions of $[(\eta^5\text{-}Cp^*)Ru(PPh_3)_2(CH_3CN)]X$ (**1**) and $[(\eta^5\text{-indenyl})Ru(PPh_3)_2(CH_3CN)]X$ (**2**) ($\eta^5\text{-}Cp^* = \eta^5\text{-}C_5Me_5$; η^5-indenyl $= \eta^5\text{-}C_9H_7$; $X = BF_4$ or PF_6) with 2,2′-bipyridine (bipy.) and 1,10-phenanthroline (phen.) in benzene or toluene yielded complexes of the type $[(\eta^5\text{-}Cp^*)Ru(PPh_3)(L_2)]X$ where L_2 = bipy, $X = BF_4$ (**3**) and L_2 = phen, $X = PF_6$ (**4**); $[(\eta^5\text{-indenyl})Ru(PPh_3)_2(L_2)]X$ where L_2 = bipy, $X = PF_6$ (**5**) and L_2 = phen, $X = PF_6$ (**6**). Complex **6** has been established by single crystal X-ray diffraction analysis. Complex **6** crystallizes in the monoclinic space group $P\ 21/c$, with $a = 14.6020\ (12)$, $b = 12.7100\ (17)$ and $c = 18.981\ (2)$ Å, $\beta = 98.982\ (9)^\circ$, $V = 3479.5\ (7)$ Å^3 and $Z = 4$. These complexes can also be prepared from reactions of $[(\eta^5\text{-}Cp^*)Ru(PPh_3)_2Cl]$ (**7**) and $[(\eta^5\text{-indenyl})Ru(PPh_3)_2Cl]$ (**8**) with the corresponding ligands in the presence of NH_4PF_6 or NH_4BF_4 in toluene. All the complexes were characterized by spectral and analytical data.

Keywords: Pentamethylcyclopentadienyl; Indenyl; Ruthenium; Molecular structures; Bipyridine; Phenanthroline

1. Introduction

The cyclopentadienyl bisphosphine ruthenium $[(\eta^5\text{-}Cp)Ru(PPh_3)_2Cl]$ chemistry has been studied extensively [1,2] with a variety of ligands. However, the corresponding analogues of Cp* and indenyl bisphosphine ruthenium chemistry have not been studied extensively due to lack of good synthetic procedures for preparation of the starting complexes. Recently, Bruce et al. [3] published a high yield synthesis of the Cp* analogue $[(\eta^5\text{-}Cp^*)Ru(PPh_3)_2Cl]$ by modifying the old procedures [4]. One can expect these complexes $[(\eta^5\text{-}Cp^*)Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-indenyl})Ru(PPh_3)_2Cl]$ to exhibit high reactivity with comparison to the cyclopentadienyl analogue due to electronic and steric factors in the case of the Cp* analogue and ring slippage nature from η^5 to η^3 and back to η^5 of the indenyl ligand [5]. In the literature there are reports [6] of the reactions of $[(\eta^5\text{-}Cp)Ru(PPh_3)_2X]$ with N-donor heterocyclic bases yielding cationic and bridged complexes depending on the halides coordinated to the ruthenium. Here we would like to report the syntheses of $[(Cp^*)Ru(PPh_3)(N\text{-base})]X$ and $[(\eta^5\text{-indenyl})Ru(PPh_3)(N\text{-base})]X$ complexes from the reaction of acetonitrile complexes **1** and **2** with bipyridine and phenanthroline heterocyclic bases and present their results.

2. Experimental

The solvents were dried by standard methods. Infrared spectra were recorded as KBr pellets using a Perkin–Elmer model 983, spectrophotometer. The ^{1}H NMR

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spectra were recorded on a Bruker ACF 300 spectrometer and referenced to external tetramethylsilane (TMS) and the coupling constants, J, are given in Hertz. ^{31}P $\{^1H\}$ NMR chemical shifts are reported relative to H_3PO_4 (85%). Elemental analyses were performed by the service center RSIC, NEHU, Shillong.

The complexes $[(\eta^5\text{-Cp*})Ru(PPh_3)_2Cl]$ [3] (**7**) and $[(\eta^5\text{-indenyl})Ru(PPh_3)_2Cl]$ [7] (**8**) were prepared by the literature methods. Ruthenium trichloride trihydrate was obtained from Arrora Matthey (P) Limited and used as such.

2.1. Preparation of $[(Cp^*)Ru(PPh_3)_2(CH_3CN)]PF_6$ (**1**)

The complex $[(Cp^*Ru(PPh_3)_2Cl]$ (0.5 g, 0.277 mmol) and NH_4PF_6 (0.15 g, 0.920 mmol) were refluxed in 20 ml of MeCN for 5 h. The orange red suspension turned yellow and a white precipitate appeared. The white precipitate was filtered off and the yellow solution was evaporated to dryness in a rotavapor. The yellow solid was dissolved in CH_2Cl_2 (5 ml) and filtered to remove excess of NH_4PF_6. It was then precipitated out in hexane to give an orange yellow complex. The product was collected and washed. Yield = 83.89%.

^1H NMR ($CDCl_3$, δ ppm): 1.3 (s, Cp*, 15H), 2.1 (s, 3H), 6.8–7.5 (m, 30H).

2.2. Preparation of $[(\eta^5\text{-indenyl})Ru(PPh_3)_2(CH_3CN)]PF_6$ (**2**)

The same procedure was used in the preparation of $[(\eta^5\text{-indenyl})Ru(PPh_3)_2(CH_3CN)]PF_6$ except the $[(\eta^5\text{-indenyl})Ru(PPh_3)_2Cl]$ complex was used instead of the $[(Cp^*)Ru(PPh_3)_2Cl]$ complex.

^1H NMR ($CDCl_3$, δ ppm): 2.1 (s, 3H), 4.2 (t, H indenyl), 3.8 (d, 2H indenyl), 6.8–7.5 (m, 34H).

2.3. Synthesis of $[(\eta^5\text{-Cp*})Ru(PPh_3)(bipy)]X$, $X = PF_6$ or BF_4 (**3**)

2.3.1. By the reaction of $[\eta^5\text{-Cp*})Ru(PPh_3)_2(CH_3CN)]PF_6$

The complex can be synthesized from the reaction of $[(\eta^5\text{-Cp*})Ru(PPh_3)_2(CH_3CN)]PF_6$ (0.1 g, 0.105 mmol) with 2,2′-bipyridine (0.018 g, 0.115 mmol) in benzene (45 ml) (the complex was initially dissolved in a minimum amount of CH_2Cl_2—3 ml) on refluxing for 2 h. The yellow solution turned into a deep red color. The solution was concentrated to about 5 ml and hexane (40 ml) was added to precipitate out the product. The red brown product was washed with hot hexane and dried. Yield: 0.07 g, 82%.

IR data (ν cm^{-1}): 527m, 694s, 746m, 924m, 1023br, 843s, 1299m, 1403m, 1435s, 1475m, 1500m, 1526m, 1551m, 1573m, 1581w, 1661m, 2915m.

^1H NMR ($CDCl_3$, δ ppm): 6.8–9.5 (m, 23H, protons of phenyl groups of triphenylphosphine and bipyridine), 1.3 (s, 15H, Cp*). ^{31}P NMR ($CDCl_3$, δ ppm): 49.6 (s, PPh_3), −147 (septet, PF_6^-).

2.3.2. By the reaction of $[(\eta^5\text{-Cp*})Ru(PPh_3)_2Cl]$

The complex $[(\eta^5\text{-Cp*})Ru(PPh_3)_2Cl]$ (0.1 g, 0.125 mmol) and 2,2′-bipyridine (0.03 g, 0.192 mmol) were refluxed for 14 h in 20 ml toluene in the presence of NH_4BF_4 (0.03 g, 0.28 mmol). The red–brown solution was concentrated to about 5 ml and was then precipitated out in hexane. The product was washed with Et_2O few times, alcohol (twice) and finally with ether. The compound was recrystallized in acetone and hexane mixture to yield orange crystals of the complex $[(\eta^5\text{-Cp*})Ru(PPh_3)(bipy)]BF_4$. Yield: 0.54 g, 57%.

IR data (ν cm^{-1}): 527m, 694s, 746m, 924m, 1023br, 1092br, 1299m, 1403m, 1435s, 1475m, 1500m, 1526m, 1551m, 1573m, 1581w, 1661m, 2915m.

^1H NMR ($CDCl_3$, δ ppm): 6.8–9.5 (m, 23H, protons of phenyl groups of triphenylphosphine and bipyridine), 1.3 (s, 15H, Cp*). ^{31}P NMR ($CDCl_3$, δ ppm): 49.6 (s, PPh_3).

2.4. Synthesis of $[(\eta^5\text{-Cp*})Ru(PPh_3)(phen)]PF_6$ (**4**)

The complex $[(\eta^5\text{-Cp*})Ru(PPh_3)_2(CH_3CN)]PF_6$ (0.1 g, 0.105 mmol) and 1,10-phenanthroline (0.025 g, 0.126 mmol) were refluxed in benzene (40 ml) (the complex was initially dissolved in minimum amount of CH_2Cl_2—3 ml) for 1 h. The initially yellow solution turned into a deep red–purple color within 10 min. The solution was evaporated to dryness and CH_2Cl_2 (5 ml) was added to dissolve the product. The dissolved compound was filtered into 50 ml of hexane to precipitate out the product. The compound was obtained by centrifuge and then washed with hexane and Et_2O. The compound was recrystallised in acetone and hexane mixture to yield orange crystals of the complex $[(\eta^5\text{-Cp*})Ru(PPh_3)(phen)]PF_6$. Yield: 0.7 g, 78%.

IR data (ν cm^{-1}): 510m, 526m, 698m, 720s, 753w, 779m, 804w, 848vs, 939w, 1028s, 1084m, 1123m, 1202m, 1285m, 1376m, 1405m, 1426m, 1441w, 1479m, 1633m, 2914w, 3435w.

^1H NMR ($CDCl_3$, δ ppm): 7.0–9.7 (m, 23H, protons of phenyl groups of triphenylphosphine and phen.), 1.45 (s, 15H, Cp*). ^{31}P NMR ($CDCl_3$, δ ppm): 49.88 (s, PPh_3), −143 (septet, PF_6^-).

2.5. Synthesis of $[(\eta^5\text{-indenyl})Ru(PPh_3)(bipy)]PF_6$ (**5**)

The complex $[(\eta^5\text{-indenyl})Ru(PPh_3)_2(CH_3CN)]PF_6$ (0.1 g, 0.108 mmol) and 2,2′-bipyridine (0.02 g, 0.128 mmol) in benzene (45 ml) (the complex was initially dissolved in minimum amount of CH_2Cl_2—3 ml) were

refluxed for 3 h. The yellow solution turned into a deep-red–brown color within 10 min. Upon concentration of the solution to about 5 ml, a brown–red compound was precipitated out. The product obtained was centrifuged and washed with hot hexane and Et_2O. The compound was recrystallised in acetone and hexane mixture to yield orange crystals of the complex [(η^5-indenyl)Ru(PPh_3)-(bipy)]PF_6. Yield: 0.74 g, 84%.

IR data (ν cm^{-1}): 510m, 529m, 696m, 720m, 747m, 845s, 993w, 1029m, 1083m, 1119w, 1200m, 1285m, 1432m, 1441m, 1479m, 1633m, 2915m, 3050m.

^1H NMR ($CDCl_3$, δ ppm): 7.0–9.6 (m, 27H, protons of phenyl groups of triphenylphosphine and bipy and indenyl groups), 4.11 (d, 2H, indenyl), 5.3 (t, 1H indenyl).

^{31}P NMR ($CDCl_3$, δ ppm): 66 (s, PPh_3), −138 (septet, PF_6^-).

2.6. Synthesis of [(η^5-indenyl)Ru(PPh_3)(phen)]PF_6 (6)

The complex was prepared by using the same procedure except phenanthroline (0.025 g, 0.126 mmol) was added instead of bipyridine. Yield: 0.78 g, 81%

IR data (ν cm^{-1}): 513m, 529m, 592w, 696s, 720m, 745m, 843s, 996w, 1090s, 1184w, 1285w, 1412m, 1480m, 1501m, 1530w, 1625m, 1937m, 2849w, 2916w, 2945w, 3050w.

^1H NMR ($CDCl_3$, δ ppm): 7.0–8.6 (m, 27H, protons of phenyl groups of triphenylphosphine and phen. and indenyl groups), 5.28 (d, 2H, indenyl), 5.7 (t, 1H indenyl). ^{31}P NMR ($CDCl_3$, δ ppm): 61 (s, PPh_3), −149 (septet, PF_6^-).

The complexes **3**, **4**, **5**, and **6** can also be prepared from the reactions of the corresponding chloro analogues **7** and **8** with N-donor bases in presence of salts NH_4BF_4 or NH_4PF_6 in refluxing toluene for 12–15 h.

3. Crystal structure determination of [(η^5-indenyl)Ru(PPh_3)(phen)]PF_6 (6)

An orange–red crystal of suitable size of **6** was mounted on the end of a glass fibre and mounted on a Nonius MACH3 diffractometer with graphite monochromatized Mo Kα ($\lambda = 0.70930$ Å) radiation for the cell determination and intensity data collection. The unit cell parameters were derived and refined by using randomly selected reflections in the θ range 8°–11°. Crystal data collection parameters are summarized in Table 1. All crystallographic calculations were performed with the use of the MAXUS [8] software. The structure was solved by direct methods [9] (SHELXS 1997). Lorentz and polarization corrections were applied. An empirical absorption correction was employed by using psi-scan where the maximum and minimum transmission factors were 1.000 and 0.972 respectively.

Table 1
Crystal data and experimental details for [(η^5-C_9H_7)Ru(PPh_3)-(phen)]PF_6

Empirical formula	$C_{39}H_{30}F_6N_2P_2Ru$
Formula weight	803.66
Temperature (K)	293(2)
Wavelength (Å)	0.70930
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	14.6020(12)
b (Å)	12.7100(17)
c (Å)	18.981(2)
β (°)	98.982(9)
Volume (Å^3)	3479.5(7)
Z	4
ρ_{calc} (Mg m^{-3})	1.534
Absorption coefficient (mm^{-1})	0.606
$F(000)$	1624
Crystal size (mm)	0.4 × 0.3 × 0.25
Data collection range (2θ) (°)	1.41–24.91
Index ranges	$0 \le h \le 17$, $0 \le k \le 15$, $-22 \le l \le 22$
Reflections collected/unique	5374/5374 [$R_{int} = 0.0000$]
Completeness to $2\theta = 24.91$	84.0%
Absorption correction	Psi-scan
Max/min transmission	1.000 and 0.972
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5374/0/571
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0367$, $wR_2 = 0.0944$
R indices (all data)	$R_1 = 0.0484$, $wR_2 = 0.1026$
Goodness-of-fit on F^2	1.033
Largest difference peak and hole (e Å^{-3})	0.734 and −0.488.

The non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were geometrically fixed and allowed to refine using a riding model. The final cycle of full-matrix least-squares refinement, based on 5374 observed reflections ($I > 2\sigma(I)$ and 571 variable parameters, converged with $R = 0.0367$ and $R_w = 0.0944$. An ORTEP drawing of **6** is shown in Fig. 1. Selected bond distances and angles are given in Table 2.

4. Results and discussion

The reaction of the chloro complexes [(η^5-Cp*)Ru(PPh_3)$_2$Cl] and [(η^5-indenyl)Ru(PPh_3)$_2$Cl] with bipyridine and phenanthroline takes place by refluxing in toluene for more than 12 h to yield cationic complexes of the type **3**–**6**, respectively. However, these reactions takes place in a more facile manner when acetonitrile complexes of the type [(η^5-indenyl)Ru(PPh_3)$_2$-(CH_3CN)]PF_6 and [(η^5-Cp*)Ru(PPh_3)$_2$(CH_3CN)]PF_6 were used.

$$[(Ar)Ru(PPh_3)_2(CH_3CN)]PF_6 + L_2 \xrightarrow[\text{toluene}]{\substack{Ar = Cp^* \text{ (1) and indenyl (2)} \\ L_2 = \text{bipy or phen}}} [(Ar)Ru(PPh_3)(L_2)]PF_6$$

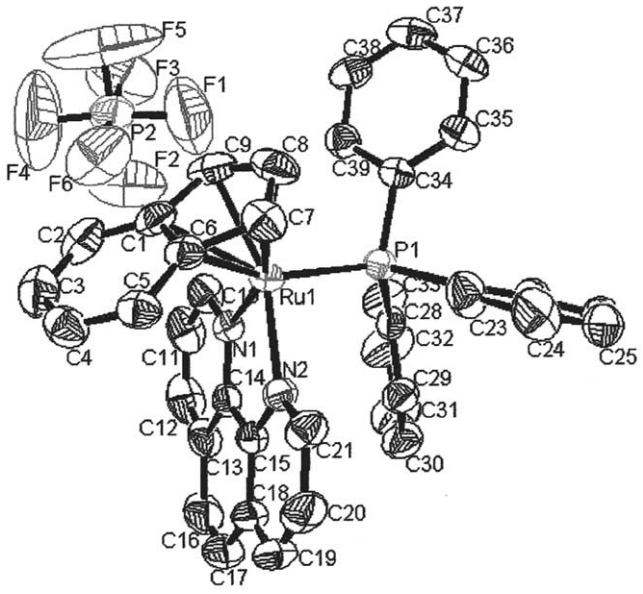

Fig. 1. ORTEP view of the complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(phen)]PF_6$ showing 30% probability thermal ellipsoids along with the atom numbering scheme.

Table 2
Bond lengths (Å) and angles (°) for $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(phen)]PF_6$

Bond lengths			
Ru(1)–N(1)	2.104(3)	P(2)–F(2)	1.579(5)
Ru(1)–N(2)	2.110(3)	N(1)–C(10)	1.340(5)
Ru(1)–C(8)	2.160(4)	N(1)–C(14)	1.366(5)
Ru(1)–C(9)	2.173(4)	N(2)–C(21)	1.339(5)
Ru(1)–C(7)	2.186(4)	N(2)–C(15)	1.355(5)
Ru(1)–P(1)	2.2875(11)	C(1)–C(2)	1.415(7)
Ru(1)–C(1)	2.293(4)	C(1)–C(6)	1.439(6)
Ru(1)–C(6)	2.301(4)	C(1)–C(9)	1.440(6)
P(1)–C(22)	1.830(4)	C(2)–C(3)	1.358(8)
P(1)–C(28)	1.833(4)	C(3)–C(4)	1.424(7)
P(1)–C(34)	1.845(4)	C(4)–C(5)	1.346(6)
P(2)–F(5)	1.470(5)	C(5)–C(6)	1.417(6)
P(2)–F(4)	1.501(6)	C(6)–C(7)	1.450(6)
P(2)–F(1)	1.526(5)	C(7)–C(8)	1.415(7)
P(2)–F(3)	1.549(4)	C(8)–C(9)	1.415(8)
P(2)–F(6)	1.572(4)		
Bond angles			
N(1)–Ru(1)–N(2)	77.46(12)	C(7)–Ru(1)–P(1)	110.02(12)
N(1)–Ru(1)–C(8)	140.84(18)	N(1)–Ru(1)–C(1)	97.50(14)
N(2)–Ru(1)–C(8)	141.18(18)	N(2)–Ru(1)–C(1)	118.96(14)
N(1)–Ru(1)–C(9)	105.17(17)	C(8)–Ru(1)–C(1)	62.10(18)
N(2)–Ru(1)–C(9)	156.17(15)	C(9)–Ru(1)–C(1)	37.50(16)
C(8)–Ru(1)–C(9)	38.1(2)	C(7)–Ru(1)–C(1)	62.66(17)
N(1)–Ru(1)–C(7)	158.85(15)	P(1)–Ru(1)–C(1)	146.38(11)
N(2)–Ru(1)–C(7)	104.85(15)	N(1)–Ru(1)–C(6)	121.70(13)
C(8)–Ru(1)–C(7)	38.00(18)	N(2)–Ru(1)–C(6)	95.50(13)
C(9)–Ru(1)–C(7)	64.24(19)	C(8)–Ru(1)–C(6)	62.08(16)
N(1)–Ru(1)–P(1)	90.52(9)	C(9)–Ru(1)–C(6)	62.59(16)
N(2)–Ru(1)–P(1)	94.64(9)	C(7)–Ru(1)–C(6)	37.60(15)
C(8)–Ru(1)–P(1)	91.56(14)	P(1)–Ru(1)–C(6)	147.62(10)
C(9)–Ru(1)–P(1)	108.91(13)	C(1)–Ru(1)–C(6)	36.50(14)

The interesting thing of these reactions are when the reactions, viz $[(\eta^5\text{-indenyl})Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-Cp*})Ru(PPh_3)_2Cl]$ with bipyridine and phenanthroline, were carried out in methanol or ethanol the organic fragment, i.e. pentamethylcyclopentadienyl and indenyl, comes out from the complex and forms simple N-base substituted coordination complexes. A similar result was observed in the case of $[(\eta^5\text{-indenyl})Ru(PPh_3)_2Cl]$ refluxed in methanol [7] at 85 °C, the complex decomposed and a mixture of ruthenium carbonyl complexes were formed, which were not characterized. Whereas a similar reaction carried out with the complex $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$ in ethanol yielded a complex of the type $[(\eta^5\text{-Cp})Ru(PPh_3)L]X$ ($X = Cl^-$, PF_6^-) [10]. In polar solvents like methanol, acetonitrile, etc. the $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$ complex readily dissociates and forms a solvated complex [11] of the type $[\eta^5\text{-Cp})Ru(PPh_3)_2(S)]^+$. A similar process is expected for these complexes $[(\eta^5\text{-Cp*})Ru(PPh_3)_2Cl]$ (**7**) and $[(\eta^5\text{-indenyl})Ru(PPh_3)_2Cl]$ (**8**). However, the process of dissociation of the metal–chloride bond in complexes **7** and **8** seems to be slower as evidenced from the reactions of these complexes with ligands in polar solvents in which the metal–chloride bond remains intact, instead the Cp* or indenyl ligands break away. Surprisingly, complexes **3**–**6** are formed when the reactions are carried out in very less polar solvents.

All these complexes were isolated as orange red crystals after recrystallization from acetone and hexane mixture. The complexes are soluble in dichloromethane, chloroform, etc. and insoluble in non-polar solvents like hexane. The IR spectra of all these complexes exhibited very strong bands due to phenyl groups of triphenylphosphine and N bases, and PF_6 exhibited a strong band for ν_{PF} at 840 cm^{-1}. Proton NMR spectra of the Cp* complexes **3** and **4** exhibited a sharp resonance at around δ 1.4 ppm for methyl protons of Cp* ligand. In the case of indenyl complexes **5** and **6** a doublet and triplet at around δ 4.7 and 5.5 ppm approximately were observed for the cyclopentadienyl ring protons of the indenyl group indicating a downfield shift from the starting complex, which is due to the cationic nature of the complex. In the parent complex $[(\eta^5\text{-indenyl})Ru(PPh_3)_2Cl]$, these protons were observed at δ 3.9 doublet and δ 4.6 triplet, respectively. This indicates that there is a downfield shift of these protons after substituting one PPh_3 with the N-donor heterocyclic ligand. The proton NMR spectra of all the complexes show a multiplet at δ 7.0–9.5 ppm due to the phenyl protons of triphenylphosphine and heterocyclic N-donor ligands. The ^{31}P NMR spectra of complexes **3** and **4** exhibited a single sharp resonance for triphenylphosphine at δ 49 ppm in contrast to the starting complex $[(\eta^5\text{-Cp*})Ru(PPh_3)_2Cl]$ at δ 38.9 ppm. In the case of the indenyl complexes, the ^{31}P NMR spectra of triphenylphosphine exhibited a single sharp resonance

around δ 66 and 61 ppm, complexes for **5** and **6**, respectively.

4.1. The structure of $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(phen)]PF_6$

The structure of complex **6** is shown in Fig. 1. The bond lengths and bond angles are listed in Table 2. The ruthenium atom is bonded to a phenanthroline ligand, one triphenylphosphine ligand and to an indenyl group through the five-member ring. The geometry about the metal atom can be regarded as distorted octahedral if the η^5-indenyl group is assumed to occupy three facial coordinated positions.

The indenyl group is clearly bonded in a pentahapto fashion to the metal, and displays the asymmetric coordination generally observed with this ligand [12]. Thus the three Ru–C bond lengths, those involving the C(7), C(8) and C(9) atoms (2.186, 2.160 and 2.173 Å, respectively) are shorter than the two to the bridging C(1) and C(6) carbon atoms (2.293 and 2.301 Å). The former three Ru–C bond lengths fall within the range of individual Ru–C distances (2.16–2.20 Å) found for structures of cyclopentadienyl ruthenium complexes [13] while the other two are outside this range. This asymmetry has been explained as slipping of η^5-bonded coordination to η^3-coordination. The five-member ring is not a regular pentagon, as observed in other complexes [14]. The benzene ring is planar, shows no significant localization of the double bonds at C(2)–C(3) (1.358 Å) and C(4)–C(5) (1.346 Å) as previously found for other indenyl complexes [12].

The Ru–P(1) bond length is 2.287 Å and falls within the usual range of Ru–P bond distances (2.20–2.43 Å) [15] as does the P–C distances [13a]. The two Ru–N bonds are almost equal (2.104 and 2.110 Å) and they fall within the usual range of ruthenium and nitrogen complexes [16]. The geometry of complex **6** is octahedral about the metal center assuming the cyclopentadienyl ring of the indenyl ligand occupyies three coordinate sites. This is evident by the near 90° bond angles between the non-indenyl ligands, N(1)–Ru–P(1) and N(2)–Ru–P(1) are 90.52° and 94.64° respectively at the metal center as seen in the crystal structure (Fig. 1).

5. Conclusions

The reactions of $[(\eta^5\text{-}Cp^*)Ru(PPh_3)_2(CH_3CN)]X$ (**1**) and $[(\eta^5\text{-indenyl})Ru(PPh_3)_2(CH_3CN)]X$ (**2**) with 2,2′-bipyridine (bipy.) and 1,10-phenanthroline (phen.) in toluene yielded complexes of the type $[(\eta^5\text{-}Cp^*)Ru(PPh_3)(L_2)]X$ and $[(\eta^5\text{-indenyl})Ru(PPh_3)_2(L_2)]X$. Complex **6** has been established by single crystal X-ray diffraction analysis. When the same reactions were carried out starting from the chloro complexes **7** and **8** in alcohol, the organic fragment, viz Cp* and indenyl, was displaced. Similar reactions carried out with the complex $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$ in alcohol yielded the desired products [10].

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 188452 for complex **6**. Copies of the 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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