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Cyclopentadienyl Ruthenium Complexes. Part I. Reactivity of some η^5-Cyclopentadienylbistriphenylphosphineruthenium(II) Complexes with N-donor Heterocyclic Ligands

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Abstract

Reactions of η^5-cyclopentadienylruthenium complexes of the type $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2X]$ (where X = Cl, Br, I, H, CN, NCS or $SnCl_3$) with N-donor ligands such as pyridine, picolines, 2,2′-bipyridine and 1,10-phenanthroline have been described for the first time. The reactions afforded cationic and neutral complexes which were characterised by elemental microanalyses, TLC, magnetic measurements, electronic, IR and ^{1}H NMR spectral data. The α-picoline did not give stable, isolable complexes and $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2H]$ failed to undergo ligand displacement reactions.

Introduction

The pronounced steric interaction and the presence of high electron density on ruthenium resulting from two bulky tertiary phosphine ligands linked to the metal ion are possibly responsible for the unusual chemistry of chloro(η^5-cyclopentadienyl)bis(trisubstituted phosphine)ruthenium [1–6]. Further, the ready substitution of one of the PR_3 molecules by other donor atoms and/or the ease of scission of the Ru–Cl bond in its methanolic solution has engendered an intense interest in its potential synthetic utility for the preparation of its extensively explored cationic and neutral substituted derivatives [7–11]. A literature survey, however, indicates that there have been no investigations on its interaction with the N-heterocyclic bases, which might alter the electron density on the ruthenium atom and also relieve the steric strain in the molecule. We therefore undertook the study of the interactions of $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2X]$ with various N-heterocyclic bases. We report herein the syntheses and a few reactions of η^5-cyclopentadienyl ruthenium complexes of the type $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2X]$ (where X = Cl, Br, I, H, CN, NCS or $SnCl_3$) with N-donor ligands such as pyridine, 2-picoline, 3-picoline, 4-picoline, 2,2′-bipyridine and 1,10-phenanthroline.

Experimental

All the chemicals used were of Analar grade. Solvents were dried and degassed before use. The reactions were carried out under dry and pure nitrogen atmosphere.

The complexes $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2Cl]$, $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2Br]$, $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2I]$, $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2H]$, $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2CN]$, $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2NCS]$, $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(SnCl_3)]$ were prepared and purified by literature methods [2, 7].

Preparation of Complexes

Reactions with pyridine, 2-picoline, 3-picoline and 4-picoline

Chloro(η^5-Cyclopentadienyl)triphenylphosphine(pyridine)ruthenium(II) Yellow orange crystals of $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2Cl]$ (100 mg, *ca.* 0.13 mmol) were heated under reflux for ten hours in about 5 cm^3 of pyridine, whereupon red crystals separated. These were centrifuged, washed with ethanol, water, ethanol and diethyl ether. The centrifugate, on concentration and addition of light petroleum ether (40–60 °C) gave a second crop of orange red microcrystals. Both samples were separately dried *in vacuo*. The complex was recrystallised from CH_2Cl_2/light petroleum (40–60 °C). It was analysed for $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)(Py)Cl]$.

The reactions of $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2X]$ where X = Br, I, H, CN, NCS or $SnCl_3$) with pyridine or picoline were carried out in a way similar to that described above, except that the appropriate complex and N-donor ligand were taken in each case. The precipitating solvent was varied in individual cases to effect the completion of the separation of the precipitate.

The reactions were not successful with 2-picoline, as no stable complex was isolated. The hydrido complex $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2H]$ resisted ligand replacement reactions even under forcing conditions.

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Reactions with 2,2'-bipyridne and 1,10-phenanthroline

Preparation of [Ru(η^5-C_5H_5)(PPh_3)L]$^+X^-$ (where L = 2,2' bipyridine or 1,10-phenanthroline, X = Cl or Br) 100 mg of the ligand L was added to a refluxing nitrogen purged solution of [Ru(η^5-C_5H_5)(PPh_3)$_2$X] (120 mg, 0.4 mmol) in ethanol (20 cm^3). The refluxing was continued for about 12 h, when the colour of the solution changed to orange-red. (It was observed that longer than 10 hours of refluxing and an excess of ligand L were mandatory for the formation of the complex.) The volume of the resulting solution was reduced to about 2 ml over a water bath, followed by the addition of excess diethyl ether (15–20 cm^3). Orange red crystals precipitated out. Scratching the walls of the reaction vessel was necessary to induce crystallisation. The orange red crystals were recrystallised from a dichloro methane/ether mixture. The complex was centrifuged out, washed with methanol, water, methanol, ether and dried *in vacuo*. The complex was analysed as [Ru(η^5-C_5H_5)(PPh_3)L]$^+$-X^-.

Preparation of [Ru_2[η^5-C_5H_5)$_2$(PPh_3)$_2$(L)X_2] (where L = 2,2'-bipyridine or 1,10-phenanthroline; X = I^-, CN^-, NCS^-, $SnCl_3^-$) A molar excess of the ligand L was added to a refluxing solution of [Ru(η^5-C_5H_5)(PPh_3)$_2$X] (100 mg, 0.1 mmol) in ethanol (25 cm^3). After 5–6 h of refluxing, the reaction mixture was reduced in volume to about 2 ml and diethyl ether was added to it after which a crystalline product was isolated. The reaction mixture could alternatively be produced by evaporating the solution to dryness, extraction with a few ml of dichloromethane, followed by the addition of light petroleum ether which yielded the same product. It was, however, found that the former method gave relatively purer complexes in the first crop. The product was separated, washed with methanol, water, methanol and ether and dried *in vacuo*. It was recrystallised from a CH_2Cl_2/light petroleum mixture.

Experiments with Ion Exchange Resins

With cation exchange resins

All the complexes described above were cationic in methanolic solution, as they were absorbed by the cation resin when passed through a cation exchange column of Dowex 50W-X8 (200–400 mesh size: Na form). It was, however, found that if the solution of these complexes was prepared in ethanol or in any other polar solvent, and the resulting solution was passed through the cation exchange column, absorption of the complexes did not take place, except in the case of [Ru(Cp)(PPh_3)(Bipy)]$^+Cl^-$, [Ru(Cp)(PPh_3)Bipy]$^+Br^-$, [Ru(Cp)(PPh_3)(o-Phen)]$^+$-Cl^- and [Ru(Cp)(PPh_3)(*o*-Phen)]$^+Br^-$, suggesting the non-ionic character in ethanol of all except those chloro- and bromo- derivatives of bipyridyl and 1,10-phenanthroline complexes. Furthermore, the latter complexes gave an immediate precipitate when methanolic or ethanolic solutions of the complexes were mixed with a concentrated aqueous solution of $NaBF_4$ or $NaBPh_4$ or KPF_6 in slight excess. The precipitated complexes were analysed for [Ru(Cp)(PPh_3)L]$^+Y^-$ (where Y^- = BF_4^-, BPh_4^- or PF_6^- and L = 2,2'-bipyridine or 1,10-phenanthroline). The filtrate obtained after filtering the above complexes analysed for the displaced Cl^- or Br^- anions. However, the same bulky anions failed to precipitate complexes where X = I, CN, NCS or $SnCl_3$ and L = 1,10-phenanthroline or 2,2'-bipyridine. The methanolic solutions of the latter complexes were mixed with a concentrated aqueous solution of $NaBF_4$ or $NaBPh_4$ or KPF_6 in slight excess. The resulting solution was concentrated to a few ml and cooled, whereupon crystalline products were separated. The crystals were centrifuged out, washed with ether and dried. The IR spectra of the isolated complexes did not show any bands corresponding to CN or NCS groups. The complexes were soluble in ether. They did, however, exhibit bands due to coordinated BF_4^- or BPh_4^- or PF_6^- groups and were analysed as [Ru(Cp)(PPh_3)L]$^+Y^-$ (Y^- = BF_4^-, BPh_4^- or PF_6^- and L = α,α'-bipyridyl or 1,10-phenanthroline).

With anion exchange resins

The ethanolic solution of the complexes when passed through a column of anion exchange resin (Dowex 1-X8, chloride form, 50–100 mesh) showed no absorption band on the column. Further addition of a solution of $NaBF_4$ or $NaBPh_4$, or KPF_6 to the eluate did not give complexes with the respective anion even on concentrating the bulk to a small volume (~2 cm^3) except those of [Ru(Cp)(PPh_3)-L]$^+X^-$ (where L = 2,2'-Bipy or 1,10-Phen; X = Cl or Br). In the latter cases, the precipitation was immediate.

Physical Measurements

The melting points of the complexes were found on a Fisher-Johns melting point apparatus.

The electronic spectra of the complexes in chloroform solution were recorded on a Cary-17D model spectrophotometer.

The IR spectra were recorded in KBr discs on a Perkin Elmer-580 spectrophotometer in the range 200–4000 cm^{-1}.

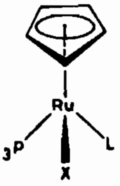
The ^{1}H NMR spectra were recorded on various HA-100 spectrophotometers, using $CDCl_3$ as solvent and TMS as internal standard.

Carbon, hydrogen and nitrogen were analysed at the central Micro-Analytical Laboratory of the I.I.T., Kanpur.

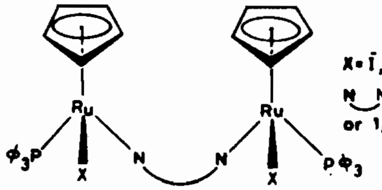
Sulphur and halogen were estimated by standard methods [12]. The phosphorus in the samples was estimated as described elsewhere [13].

Results and Discussion

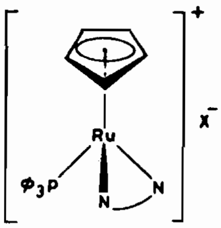
Reactions of the complexes described in the literature, $[Ru(Cp)(PPh_3)_2X]$ (X = Cl, Br, I, CN, NCS, $SnCl_3$) with N-heterocyclic bases in ethanolic solvent led to the generation of substitution complexes. Table I lists their empirical formulae arrived at using the microanalytical data (given therein) together with some of their physical properties. These are air-stable, yellow to yellowish-red crystalline solids, highly soluble in organic polar solvents like CH_2Cl_2, $CHCl_3$, *etc.* and to a limited extent in protic solvents like alcohols. In each synthetic reaction, the recovery of triphenylphosphine nearly equivalent to one mol per mol of the starting complex suggested the substitution of one molecule of PPh_3 by the heterocyclic base.



An interesting aspect of these reactions is the behavioural difference of the chloro- or bromo-derivative of $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2X]$ with bipyridyl or 1,10-phenanthroline which resulted in the formation of the cationic complexes $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)L]^+X^-$. The complexes of the remaining anions gave neutral complexes $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)(L)_{1/2}X]$ (where L = 2,2′-bipyridyl or 1,10-phenanthroline). It appears that electronic effects play a major role in the formation of these species.



The complexes $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)(L)Cl]$ can be converted into $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)(L)Br]$, $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)(L)I]$, $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)(L)CN]$, $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)(L)NCS]$ and $[Ru(\eta^5\text{-}C_5H_5)(L)SnCl_3]$ by refluxing in methanol with a slight molar excess of NaBr, NaI, KCN, KNCS or $SnCl_2$, respectively. There is a likelihood [14] that the reaction intermediate in methanol is a cationic species, $[Ru(Cp)(MeOH)(PPh_3)(L)]^+$, which undergoes substitution reactions under relatively mild conditions yielding $[Ru(Cp)(PPh_3)(L)X]$ in the presence of an added anion. However, refluxing the mixed ligand products $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)(L)X]$ with excess PPh_3 in ethanol for a longer period did not give the parent complex $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2X]$. TLC measurements confirmed the presence of $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)(L)X]$ as a single major product.



The IR spectra of all the compounds exhibited two slightly broad bands of medium intensity in the region 820–850 cm^{-1} and 420 cm^{-1} corresponding to out-of-plane bending and skeletal modes of the C_5H_5 ring, respectively. In order to arrive at any logical correlation, the shifts in the positions of these bands (10–15 cm^{-1}) were found to be rather small in all the complexes excepting those in $[Ru(Cp)(PPh_3)L]^+X^-$ (where L = 2,2′-bipy or 1,10-phen, X = Cl or Br) where the shifts were observed to be large towards higher wavenumbers (850 and 440 cm^{-1}). (Interestingly, there has been found to be one to one correspondence between these shifts and those found for the downfield shifts of C_5H_5 proton signals in their ^1H NMR spectra.) In addition to these bands, the characteristic bands of triphenylphosphine, pyridine, picoline, 2,2′-bipyridine or 1,10-phenanthroline [15–18] were also present in the spectra. Further, the IR spectra of all the complexes displayed a characteristic pattern of three bands decreasing in intensity between 535 cm^{-1} and 495 cm^{-1} (associated with the triphenylphosphine ligand) which suggests the presence of only one coordinated triphenylphosphine molecule in the complex [19]. It supports the displacement of one of the triphenylphosphine groups by the N-donor ligand. The cyanato and thiocyanato complexes showed absorption at 2050 and 2100 cm^{-1}, respectively indicative of the presence of the CN and NCS groups [20–23].

^1H NMR spectra of all the complexes showed a sharp resonance in the region δ 4.0–5.0. The sharp singlet in this region is characeteristic of π-bonded cyclopentadiene. The aromatic groups on the triphenylphosphine and donor ligands showed broad complex resonances in the usual range of

TABLE I. Characterisation Data.

Complex	Colour[a]	Analysis, Found (Calcd.), %						λ_{nm}^{max} (in $CHCl_3$)	IR bands (cm^{-1}) (C_5H_5)	C_5H_5 ^1H NMR (δ ppm)b
		C	H	X	S	N	P			
1	2	3	4	5	6	7	8	9	10	11
[Ru(Cp)(PPh_3(Py)Cl] (m.p. 135 °C (d))	R	62.2 (61.9)	4.5 (4.6)	6.1 (6.5)	–	2.5 (2.6)	5.6 (5.7)	595,465	832	4.10
[Ru(Cp)(PPh_3)(β-Pic)Cl] (m.p. 144–45 °C (d))	Y	63.1 (62.5)	4.8 (4.9)	5.9 (6.4)		2.5 (2.5)	5.6 (5.6)	530,430	837	4.12
[Ru(Cp)(PPh_3)(γ-Pic)Cl] (m.p. 148 °C)	YB	62.2 (62.5)	4.8 (4.9)	5.9 (6.4)	–	2.4 (2.5)	5.5 (5.6)	530,425	837	4.12
[Ru(Cp)(PPh_3)(Bipy)]$^+Cl^-$ (m.p. 240 °C)	O	63.7 (63.9)	4.5 (4.6)	5.8 (5.7)	–	4.4 (4.5)	5.1 (5.0)	600,410	840	4.50
[Ru(Cp)(PPh_3)(*o*-Phen)]$^+Cl^-$ (m.p. 235–37 °C)	O	65.9 (65.3)	4.3 (4.4)	5.9 (5.5)	–	4.5 (4.4)	4.9 (4.8)	595,410, 400	843	4.84
[Ru(Cp)(PPh_3)(Py)Br] (m.p. 142 °C)	GB	57.5 (57.2)	4.4 (4.3)	13.3 (13.6)	–	2.5 (2.4)	5.3 (5.3)	600,470, 400	830	4.12
[Ru(Cp)(PPh_3)(β-Pic)Br] (m.p. 134 °C)	O	57.2 (57.9)	4.4 (4.5)	13.4 (13.3)	–	2.4 (2.3)	5.1 (5.2)	595,460, 420	810	4.10
[Ru(Cp)(PPh_3)(γ-Pic)Br] (m.p. 136 °C)	O	57.3 (57.9)	4.5 (4.5)	13.3 (13.3)	–	2.3 (2.3)	5.1 (5.2)	590,465, 420	810	4.10
[Ru(Cp)(PPh_3)(Bipy)]$^+Br^-$ (m.p. 245 °C)	O	59.8 (59.6)	4.1 (4.2)	11.9 (12.0)	–	4.1 (4.2)	4.6 (4.7)	610,470	830	4.70
[Ru(Cp)(PPh_3)(*o*-Phen)]$^+Br^-$ (m.p. 250–52 °C)	O	60.0 (60.9)	4.0 (4.1)	11.8 (11.6)	–	4.1 (4.1)	4.4 (4.5)	605,470, 430	840	4.85
[Ru(Cp)(PPh_3)(Py)I] (m.p. 232 °C (d))	B	53.0 (53.0)	3.8 (3.9)	19.0 (20.0)	–	2.3 (2.2)	4.8 (4.9)	650,510, 420	832	4.20
[Ru(Cp)(PPh_3)(β-Pic)I] (m.p. 162 °C (d))	B	53.7 (53.7)	4.3 (4.2)	19.6 (19.6)	–	2.1 (2.2)	4.9 (4.8)	650,500, 440	830	4.15
[Ru(Cp)(PPh_3)(γ-Pic)I] (m.p. 164 °C)	B	53.9 (53.7)	4.2 (4.2)	19.6 (19.6)	–	2.2 (2.2)	4.9 (4.8)	650,460	830	4.13
[Ru(Cp)(PPh_3)$(Bipy)_{1/2}$I] (m.p. 172 °C)	BO	52.9 (53.1)	3.9 (3.8)	19.2 (20.1)	–	2.3 (2.2)	4.8 (4.9)	530,440, 400	835	4.18
[Ru(Cp)(PPh_3)$(o\text{-Phen})_{1/2}$I] (m.p. 245 °C)	O	53.9 (54.0)	3.8 (3.7)	19.3 (19.7)		2.2 (2.2)	4.7 (4.8)	520,420	830	4.18
[Ru(Cp)(PPh_3)(Py)(CN)] (m.p. 240–42 °C)	Y	65.3 (65.3)	4.6 (4.7)	–	–	5.3 (5.3)	5.8 (5.8)	550,460	855 ν_{CN} 2042	4.37
[Ru(Cp)(PPh_3)(β-Pic)(CN)] (m.p. 240 °C)	Y	65.7 (65.8)	4.8 (4.9)	–	–	5.2 (5.1)	5.9 (5.7)	470,360	850 ν_{CN} 2050	4.36
[Ru(Cp)(PPh_3)(γ-Pic)(CN)] (m.p. 235 °C)	Y	65.8 (65.8)	4.8 (4.5)	–	–	5.2 (5.1)	5.9 (5.7)	480,360	850 ν_{CN} 2050	4.35
[Ru(Cp)(PPh_3)$(Bipy)_{1/2}$(CN) (m.p. 250 °C)	Y	65.4 (65.4)	4.4 (4.5)	–	–	5.4 (5.3)	5.9 (5.8)	480,360	850 ν_{CN} 2080	4.35
[Ru(Cp)(PPh_3)$(o\text{-phen})_{1/2}$(CN)] (m.p. 265 °C)	Y	65.8 (66.2)	4.3 (4.4)	–	–	5.0 (5.1)	5.8 (5.7)	535,480 405	852 ν_{CN} 2054	4.25
[Ru(Cp)(PPh_3)(Py)(NCS)] (m.p. 195 °C)	Y	61.9 (61.6)	4.3 (4.4)	–	5.9 (5.7)	5.1 (5.0)	5.4 (5.5)	560,525	830 ν_{CN} 2060	4.20
[Ru(Cp)(PPh_3)(β-Pic)(NCS)] (m.p. 160 °C)	GY	62.0 (62.2)	4.8 (4.7)	–	5.6 (5.5)	4.9 (4.8)	5.3 (5.4)	590,500, 445	835 ν_{CN} 2090	4.15
[Ru(Cp)(PPh_3)(γ-Pic)(NCS)] (m.p. 185–88 °C)	Y	62.5 (62.2)	4.8 4.7)	–	5.7 (5.5)	4.9 (4.8)	5.5 (5.4)	595,505, 420	835 ν_{CN}2090	4.15

(continued on facing page)

TABLE I *(continued)*

Complex	Colour[a]	Analysis, Found (Calcd.), %						λ_{nm}^{max} (in $CHCl_3$)	IR bands (cm^{-1}) (C_5H_5)	C_5H_5 ^1H NMR (δ ppm)[b]
		C	H	X	S	N	P			
1	2	3	4	5	6	7	8	9	10	11
$[Ru(Cp)(PPh_3)(Bipy)_{1/2}(NCS)]$ (m.p. 193 °C)	YB	62.0 (61.7)	4.2 (4.3)	–	5.8 (5.7)	5.1 (5.0)	5.6 (5.5)	595,450, 410	832 ν_{CN} 2050	4.20
$[Ru(Cp)(PPh_3)(o\text{-phen})_{1/2}(NCS)]$ (m.p. 203 °C)	OB	61.9 (62.5)	4.3 (4.2)	–	5.4 (5.5)	4.8 (4.9)	5.5 (5.4)	595,490, 460,405	830 ν_{CN} 2040	4.16
$[Ru(Cp)(PPh_3)(Py)(SnCl_3)]$ (m.p. 210 °C)	O	45.9 (45.9)	3.5 (3.4)	14.8 (14.5)	–	1.8 (1.9)	4.3 (4.2)	580,470	852	4.60
$[Ru(Cp)(PPh_3)(\beta\text{-Pic})(SnCl_3)]$ (m.p. 212 °C)	Y	46.9 (46.6)	3.6 (3.6)	14.1 (14.3)	–	1.8 (1.9)	4.3 (4.2)	590,480	855	4.50
$[Ru(Cp)(PPh_3)(\gamma\text{-Pic})(SnCl_3)]$ (m.p. 208–10 °C)	Y	46.7 (46.7)	3.6 (3.6)	13.8 (14.3)	–	1.8 (1.9)	4.4 (4.2)	595,480, 415	855	4.50
$[Ru(Cp)(PPh_3)(Bipy)_{1/2}(SnCl_3)]$ (m.p. 210 °C)	O	46.0 (46.0)	3.4 (3.3)	15.0 (14.6)	–	1:9 (1.9)	4.1 (4.2)	570,450	852	4.50
$[Ru(Cp)(PPh_3)(o\text{-phen})_{1/2}(SnCl_3)]$ (m.p. 206 °C)	O	46.6 (46.8)	3.1 (3.2)	14.8 (14.3)	–	1.8 (1.9)	4.1 (4.2)	580,470	850	4.55
$[Ru(Cp)(PPh_3)(2,2'\text{-Bipy})]^+ BF_4^-$ (m.p. 272 °C)	OY	59.2 (59.0)	4.3 (4.2)	–	–	4.3 (4.2)	4.8 (4.6)	580,470	850	4.81
$[Ru(Cp)(PPh_3)(2,2'\text{-Bipy})]^+\text{-}BPH_4^-$ (m.p. 280 °C)	O	75.5 (75.7)	5.2 (5.3)	–	–	3.2 (3.1)	3.5 (3.4)	560,430	850	4.92
$[Ru(Cp)(PPh_3)(2,2'\text{-Bipy})]^+\text{-}PF_6^-$ (m.p. 278 °C)	OY	54.6 (54.3)	3.7 (3.8)	–	–	3.9 (3.8)	8.6 (8.5)	582,468	848	4.83
$[Ru(Cp)(PPh_3)(o\text{-phen})]^+BF_4^-$ (m.p. 268 °C)	OY	60.7 (60.4)	4.1 (4.0)	–	–	4.1 (4.0)	4.6 (4.5)	585,460	846	4.85
$[Ru(Cp)(PPh_3)(o\text{-phen})]^+BPh_4^-$ (m.p. 274 °C)	O	76.7 (76.4)	5.3 (5.2)	–	–	3.1 (3.0)	3.4 (3.3)	562,435	850	4.94
$[Ru(Cp)(PPh_3(o\text{-phen})]PF_6^-$ (m.p. 278 °C)	OY	55.7 (55.8)	3.8 (3.7)	–	–	3.5 (3.7)	8.5 (8.2)	580,460	848	4.81

[a] R = Red,, Y = Yellow, YB = Yellowish Brown, O = Orange, B = Brown, BO = Brownish Orange, GY = Greenish Yellow, GB = Greenish Brown, OB = Orange Brown, OY = Orange Yellow. [b] Solvent $CDCl_3$. Aromatic protons of the other coligands appeared in the region δ 7–8 as broad multiplets, and in the case of picolines additional signals in the region δ 1.8–2.0 were observed due to the methyl protons.

δ 7–8 for the C_6H_5 protons. The intensity ratio of the signals corresponded to the ratio of the number of hydrogen atoms of the cyclopentadienyl anion and those of one triphenylphosphine molecule plus the hydrogen atoms present in pyridine, picoline, 2,2′-bipyridine or 1,10-phenanthroline. The protons of the N-donor ligands gave signals in the region of p-C_6H_5 proton signals, and as a result the resonance observed in this region was a broad multiplet in all the cases. In the case of picoline complexes, an additional signal in the region δ 1.7–2.0 was noticed for the methyl protons. There are two interesting aspects concerning the position of the cyclopentadienyl band in different complexes. (1) A slight downfield shift in the spectra of all the complexes (δ ~ 4.2) except $[Ru(Cp)(PPh_3)(L)]^+X^-$ (L = bipy, o-phen; X = Cl, Br) compared to that in $[Ru(Cp)(PPh_3)_2X]$ (δ 4.08). (2) A larger shift (δ 4.75–4.8) in the spectra of cationic complexes. These values match very well those obtained in all the similar Ru–Cp cationic complexes [1–11].

The first aspect implies an increase of electron density at the ruthenium center which will make the diamagnetic induced current stronger and lead to increased paramagnetic shielding of C_5H_5 protons.

The effective increase of electron density could be due to the decrease in the degree of π-backbonding by substituting a better π-acceptor (PPh_3), with a relatively poor one (heterocyclic molecule). The other effect may possibly be caused by the presence of the charge on the ruthenium center which may act as an electron withdrawing group, decreasing the π-electron density at the carbon atoms of the cyclopentadienyl ring and thereby shifting the band

TABLE II. IR and ^{1}H NMR Data.

Complex	ν_{CN} (cm^{-1})^a	C_5H_5 ^{1}H NMR δ ppm^b
$[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(CN)]$	2038	4.10
$[Ru(\eta^5\text{-}C_5H_5)(PPh_3)(Py)(CN)]$	2045	4.37
$[Ru(\eta^5\text{-}C_5H_5)(PPh_3)(\beta\text{-pic})(CN)]$	2045	4.36
$[Ru(\eta^5\text{-}C_5H_5)(PPh_3)(\gamma\text{-pic})(CN)]$	2045	4.35
$[Ru(\eta^5\text{-}C_5H_5)(PPh_3)(Bipy)_{1/2}(CN)]$	2020	4.35
$[Ru(\eta^5\text{-}C_5H_5)(PPh_3)(o\text{-phen})_{1/2}(CN)]$	2050	4.25

^{a}Recorded as KBr discs. ^{b}Solvent $CDCl_3$.

downfield because of the local diamagnetic shielding effect.

The presence of a unipositive charge on the complex $[Ru(Cp)(PPh_3)L]^+X^-$ gains further support from the ion exchange and IR spectral studies.

Magnetic Moments and Electronic Spectra

The complexes were found to be diamagnetic, indicating spin pairing. In all of them the symmetry of the donor atoms around the metal center may be considered to be distorted octahedral, based upon the assumption that the cyclopentadienyl group occupies three coordination sites, or distorted tetrahedral if the perpendicular axis of the C_5 ring is considered to occupy one position. The diamagnetism of the complexes is, however, strongly suggestive of the former alternative, because of the definite possibility of there being spin free complexes in a tetrahedral environment. In the discussion of the electronic spectra, we have therefore preferred a distorted octahedral environment of the ligand field around the metal ion.

The positions of the absorption bands in the UV and visible regions of the electronic spectra of the complexes are tabulated in Table II. Since the metal ion in all the complexes is bonded with heterocyclic bases having delocalized π-electrons, the low spin d^6 configuration of the metal ion provides filled orbitals of the proper symmetry to interact with relatively low energy, unoccupied π-orbitals on the ligand, L. The fairly intense bands between 450 nm and 650 nm could therefore be attributed to metal to ligand charge transfer (MLCT) transition ($t_{2g} \rightarrow \pi^*$) [25–28]. The energy of these transitions varied with the ability of the anionic ligand to act as π-acceptor or donor and also with their positions in the spectrochemical series.

Although the variation of the MLCT band with the nature of the heterocyclic base is not very regular, it is however observed that there is a tendency for the band position to shift toward blue from pyridines to 1,10-phenanthroline. It could be that, because of greater delocalisation of π-electron density in 1,10-phenanthroline or 2,2'-bipyridine, π^* orbitals of the bases may come closer to t_{2g} orbitals in energy, leading to a greater interaction between them (t_{2g} and π^*) which will result in an increase of ΔE between ($t_{2g} + \pi^*$) and ($t_{2g} - \pi^*$) orbitals with a consequent blue shift in band position in these complexes.

It is interesting to note that 2-picoline did not undergo any substitution reactions because of the steric hindrance. In every reaction an oily product was obtained from which no pure product could be isolated. We believe that the oily product was a mixture of a number of compounds formed as a result of decomposition of the reactant complex under stringent conditions.

Analogously, the hydrido derivative of the cyclopentadienyl complex of ruthenium did not react with N-heterocyclic bases and in every reaction the product found was the initial hydrido complex. Possibly, the hydride ion, being very small, may be difficult to substitute by the bases which might enhance the steric hindrance in an already more sterically hindered molecule, $[R(\eta^5\text{-}C_5H_5)(PPh_3)_2\text{-}H]$ [1–6].

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