Journal of Organometallic Chemistry 696 (2011) 758-763

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Heteroleptic half-sandwich Ru(II), Rh(III) and Ir(III) complexes based on 5-ferrocenyldipyrromethene

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ARTICLE INFO

Article history: Received 5 July 2010 Received in revised form 28 September 2010 Accepted 28 September 2010 Available online 14 October 2010

Keywords: Ruthenium(II) Rhodium(III) Iridium(III) Piano-stool complexes 5-Ferrocenyl-dipyrromethene

1. Introduction

Considerable current attention has been paid towards the synthesis and characterization of complexes based on mesosubstituted dipyrrin ligands owing to their ease of synthesis, rich optical properties and tendency to form stable complexes with a variety of metal ions [1,2]. Presence of two pyrrolic nitrogen donors in planar dipyrrin core and functionalized meso-substituents enables the dipyrrins to display wide applications in coordination chemistry [1]. The meso-substituted dipyrrins are easily prepared by condensation of aldehydes with an excess of pyrrole followed by oxidation and their properties can be modified by introducing electron withdrawing/ donating substituents, which strongly influences their electrochemical and optical properties. Although, a large number of homoleptic dipyrrin complexes have been prepared and thoroughly studied, the chemistry of heteroleptic dipyrrin complexes have not been explored to the same extent [3–7]. Complexes possessing dipyrrin core along with other ligands offer interesting substitution chemistry and great prospective in the syntheses of new materials. In addition, heteroleptic organometallic compounds containing η^6 -arene ruthenium and η^5 -C₅Me₅ rhodium/iridium complexes have attracted attention of many research groups because of their catalytic potential and wide applications as precursor in the synthesis of other Ru(II), Rh(III), and Ir(III) complexes [8,9]. In this context, dimeric arene ruthenium [{(η^6 -arene)Ru(μ -Cl)Cl}₂] (η^6 -arene = benzene and its

ABSTRACT

The synthesis and characterization of heteroleptic complexes with the formulations $[(\eta^6\text{-arene})RuCl(fcdpm)]$ ($\eta^6\text{-arene} = C_6H_6$, $C_{10}H_{14}$) and $[(\eta^5\text{-}C_5Me_5)MCl(fcdpm)]$ (M = Rh, Ir; fcdpm = 5-ferrocenyldipyrromethene) have been reported. All the complexes have been characterized by elemental analyses, IR, ¹H NMR and electronic spectral studies. Structures of $[(\eta^6\text{-}C_6H_6)RuCl(fcdpm)]$ and $[(\eta^6\text{-}C_{10}H_{14})RuCl(fcdpm)]$ have been determined crystallographically. Chelating monoanionic linkage of fcdpm to the respective metal centres has been supported by spectral and structural studies. Further, reactivity of the representative complex $[(\eta^6\text{-}C_{10}H_{14})RuCl(fcdpm)]$ with ammonium thiocyanate (NH₄SCN) and triphenylphosphine (PPh₃) have been examined.

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derivatives) and structurally analogous pentamethyl-cyclopentadienyl rhodium/iridium complexes [$\{(\eta^5-C_5Me_5)M(\mu-Cl)Cl\}_2$] (M = Rh or Ir) have proved to be indispensable starting materials [10–13].

Transition metal complexes containing a redox active ferrocene moiety find potential applications in catalysis [14,15], designing of new non-linear optical materials [16], biologically active compounds [17], and as anti-cancer agents [18]. Although, 5-ferrocenyl-dipyrromethane possessing a ferrocenyl moiety as the mesosubstituent was reported by Moriarty et al., in 1999, its coordination chemistry has scarcely been explored [19]. With an objective of developing the organometallic chemistry of fcdpm, reactivity of arene ruthenium [{(η^6 -arene)Ru(μ -Cl)Cl}₂] (η^6 -arene = C₆H₆, C₁₀H₁₄) and structurally analogous rhodium and iridium complexes $[{(\eta^5-C_5Me_5)M(\mu-Cl)Cl}_2]$ (M = Rh or Ir) have been examined with fcdpm. Through this work we present the syntheses and characterization of η^6 -arene ruthenium(II), η^5 -pentamethyl-cyclopentadienyl rhodium(III)/iridium(III) complexes and reactivity of representative ruthenium complex $[(\eta^6-C_{10}H_{14})RuCl(fcdpm)]$ with monodentate ligands like SCN-, PPh3. Also, we describe herein single crystal X-ray structures of $[(\eta^6-C_6H_6)RuCl(fcdpm)]$ and $[(\eta^6-C_6H_6)RuCl(fcdpm)]$ C10H14)RuCl(fcdpm)].

2. Experimental

2.1. Materials and physical measurements

The solvents were rigorously purified and dried by standard procedures prior to their use [20]. Hydrated ruthenium(III) chloride,



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⁰⁰²²⁻³²⁸X/\$ – see front matter @ 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.jorganchem.2010.09.070



Scheme 1. Synthesis of complexes of 1-4.

rhodium(III) chloride, iridium(III) chloride, α -phellanderene, 1,3-hexadiene, pentamethylcyclopentadiene, 2,3-dicloro-5,6-dicyano-1,4-benzoquinone (DDQ), ferrocenylcarboxaldehyde, pyrrole, silver trifluoromethanesulfonate, triphenylphosphine and ammonium thiocyanate (all Aldrich) were used as received without further purifications. The precursor complexes [{(η^6 -arene)Ru(μ -Cl)Cl}₂] (η^6 -arene = C₆H₆ [21], C₁₀H₁₄ [22]), [{(η^5 -C₅Me₅)M(μ -Cl)Cl}₂] (M = Rh [23] or Ir [24]) and the ligand 5-ferrocenyldipyrromethane were prepared and purified following the literature procedures [25]. Elemental analyses for C, H and N were performed on an Exeter Analytical Inc. Model CE-440 Elemental Analyzer. IR and electronic absorption spectra were acquired on a Varian 3300 FTIR and Shimadzu UV-1700 series spectrophotometers, respectively. ¹H NMR spectra were recorded on a JEOL AL 300 NMR spectrometer at r.t. in CDCl₃ using TMS as an internal reference.

2.2. Syntheses

2.2.1. Preparation of $[(\eta^6 - C_6H_6)RuCl(fcdpm)]$ **1**

To an ice-cold solution of 5-ferrocenyldipyrromethane (0.165 g, 0.5 mmol) in CHCl₃ (75 mL), DDQ (0.114 g, 0.5 mmol) dissolved in benzene (50 mL) was added slowly with stirring over a period of 1 h. After TLC confirmed complete consumption of the starting material, solvent was removed under reduced pressure and dark red residue redissolved in CHCl₃/MeOH (60 mL; 1:1 v/v) and filtered. Triethylamine (0.50 mL) and $[{(\eta^6-C_6H_6)Ru(\mu-Cl)Cl}_2]$ (0.125 g, 0.25 mmol) were successively added to the filtrate and heated under reflux overnight. It was allowed to cool to r.t. and concentrated to dryness under reduced pressure to afford a black solid which was purified by column chromatography (SiO₂; CHCl₃ with 10% hexane). Second bright orange band afforded the desired product $[(\eta^6-C_6H_6)RuCl(fcdpm)]$ as lustrous green solid. Yield: 0.111 g, 41%. Anal. Calc. for C25H21ClN2FeRu: C, 55.42; H, 3.91; N, 5.17. Found: C, 55.74; H, 3.86; N, 5.34%. IR (KBr pellets, cm⁻¹): 480, 667, 728, 770, 810, 885, 993, 1034, 1190, 1204, 1240, 1338, 1393, 1460, 1556, 2912, 3091. ¹H NMR (δ ppm): 4.17 (s, 5H), 4.47 (s, 2H), 4.76 (s, 2H), 5.58 (s, 6H), 6.49 (d, 2H, J = 3.3 Hz), 7.66 (d, 2H, J = 3.6 Hz), 8.01 (s, 2H). UV-vis. (CH₂Cl₂, λ_{max} nm, ϵ M⁻¹ cm⁻¹): 508 (3.21×10^4) , 436 (1.25×10^4) , 337 (1.62×10^4) , 230 (3.83×10^4) .

2.2.2. Preparation of $[(\eta^6 - C_{10}H_{14})RuCl(fcdpm)]$ 2

Complex **2** was synthesized following the above procedure using $[\{(\eta^6-C_{10}H_{14})Ru(\mu-Cl)Cl\}_2]$ (0.153 g, 0.25 mmol) in place of $[\{(\eta^6-C_{6}H_6)Ru(\mu-Cl)Cl\}_2]$. Yield: 0.135 g, 45%. Anal. Calc. for C₂₉H₂₉ClN₂FeRu: C, 58.25, H, 4.89; N, 4.69%. Found: C, 58.45, H, 4.86; N, 4.83%. IR (KBr pellets, cm⁻¹): 474, 717, 766, 810, 890, 993, 1034, 1190, 1204, 1248, 1343, 1378, 1447, 1557, 2917, 3092. ¹H NMR (δ ppm); 1.15 (d, 6H, *J* = 6.9), 2.24 (s, 3H), 2.42 (m, 1H), 4.14 (s, 5H), 4.45 (s, 2H), 4.72 (s, 2H), 5.25 (s, 4H), 6.47 (d, 2H, *J* = 3.3 Hz), 7.58 (d, 2H, *J* = 3.6 Hz), 7.90 (s, 2H). UV–vis. (CH₂Cl₂, λ_{max} nm, ϵ M⁻¹ cm⁻¹): 506 (3.10 × 10⁴), 434 (1.70 × 10⁴), 340 (1.99 × 10⁴), 248 (3.06 × 10⁴), 230 (3.83 × 10⁴).

2.2.3. Preparation of $[(\eta^5 - C_5 Me_5)RhCl(fcdpm)]$ **3**

This complex was prepared following the above procedure for **1** except that $[\{(\eta^5-C_5Me_5)Rh(\mu-Cl)Cl\}_2]$ (0.154 g, 0.25 mmol) was used in place of $[\{(\eta^6-C_6H_6)Ru(\mu-Cl)Cl\}_2]$. Yield: 0.117 g, 39%. Anal. Calc. for $C_{29}H_{30}ClN_2FeRh$: C, 57.98, H, 5.03; N, 4.66%. Found: C, 57.78, H, 4.98; N, 4.54%. IR (KBr pellets, cm⁻¹): 474, 667, 720, 770, 820, 890, 990, 1030, 1185, 1204, 1248, 1338, 1393, 1460, 1533, 1557, 2920, 3094. ¹H NMR (δ ppm): 1.52 (s, 15H), 4.16 (s, 5H), 4.47 (s, 2H), 4.75 (s, 2H), 6.48 (d, 2H, J = 3.9 Hz), 7.57 (d, 2H, J = 3.9 Hz), 7.60 (s, 2H). UV–vis. (CH₂Cl₂, λ_{max} nm, ϵ M⁻¹ cm⁻¹): 521 (3.08 × 10⁴), 412 (1.89 × 10⁴), 341 (2.41 × 10⁴), 250 (3.50 × 10⁴), 231 (4.81 × 10⁴).

2.2.4. Preparation of $[(\eta^5 - C_5 M e_5) IrCl(fcdpm)]$ **4**

Complex **4** was prepared following the above procedure for **1** except that $[\{(\eta^5-C_5Me_5)Ir(\mu-CI)CI\}_2]$ (0.199 g, 0.25 mmol) was used in place of $[\{(\eta^6-C_6H_6)Ru(\mu-CI)CI\}_2]$. Yield: 0.138 g, 40%. Anal. Calc. for $C_{29}H_{30}CIN_2FeIr$: C, 50.47, H, 4.38; N, 4.06%. Found: C, 50.52, H, 4.43; N, 4.12%. IR (KBr pellets, cm⁻¹): 473, 667, 714, 771, 820, 893, 990, 1032, 1185, 1205, 1248, 1339, 1391, 1460, 1535, 1555, 2922, 3094. ¹H NMR (δ ppm): 1.51 (s, 15H), 4.17 (s, 5H), 4.48 (s, 2H), 4.75 (s, 2H), 6.46 (d, 2H, J = 3.9 Hz), 7.58 (d, 2H, J = 3.9 Hz), 7.62 (s, 2H). UV–vis. (CH₂Cl₂, λ_{max} nm, ϵ M⁻¹ cm⁻¹): 507 (2.48 × 10⁴), 432 (2.01 × 10⁴), 343 (2.52 × 10⁴), 253 (3.79 × 10⁴), 229 (5.32 × 10⁴).

2.2.5. Preparation of $[(\eta^6 - C_{10}H_{14})Ru(SCN)(fcdpm)]$ 5

To a solution of $[(\eta^6-C_{10}H_{14})RuCl(fcdpm)]$ (0.150 g, 0.25 mmol) in dry acetone (10 mL), solid NH₄SCN (0.019 g, 0.25 mmol) was



Scheme 2. Synthesis of complexes (i) NH₄SCN/acetone, (ii)AgSO₃CF₃/PPh₃/acetone.



Fig. 1. Electronic absorption spectra of the complexes.

added and stirred at room temperature for 3 h. It was filtered and concentrated to dryness under reduced pressure. The residue was extracted with dichloromethane (7 mL) and filtered to remove solid NH₄Cl. Addition of an excess of hexane to the filtrate afforded orange colored product which filtered, washed with diethyl ether and dried under vacuum. Yield: 0.114 g, 74%. Anal. Calc. for C₃₀H₂₉N₃SFeRu: C, 58.07; H, 4.71; N, 6.77%. Found: C, 58.19; H, 4.78; N, 6.63%. IR (KBr pellets, cm⁻¹): 470, 720, 765, 815, 890, 992, 1034, 1190, 1204, 1246, 1340, 1378, 1459, 1550, 2100, 2920, 3090. ¹H NMR (δ ppm): 1.09 (d, 6H, *J* = 6.6 Hz), 2.28 (s, 3H), 2.37 (m, 1H), 4.14 (s, 5H), 4.46 (s, 2H), 4.76 (s, 2H), 5.25 (s, 4H), 6.53 (s, 2H), 7.65 (d, 2H, *J* = 4.8 Hz), 7.87 (s, 2H). UV–vis. (CH₂Cl₂, λ_{max} nm, ϵ M⁻¹ cm⁻¹): 506 (3.12 × 10⁴), 438 (1.74 × 10⁴), 343 (2.16 × 10⁴), 231 (6.98 × 10⁴).

2.2.6. Preparation of $[(\eta^6-C_{10}H_{14})Ru(PPh_3)(fcdpm)]SO_3CF_3$ **6**

To a solution of complex **2** (0.150 g, 0.25 mmol) in dry acetone (30 mL), AgSO₃CF₃ (0.065 g, 0.25 mmol) was added and stirred for 2 h at r.t. It was filtered through celite to remove the white precipitate of silver chloride. Triphenylphosphine (0.066 g, 0.25 mmol) was added to the filtrate and stirred at r.t. for 4 h. The solvent was

 Table 1

 Crystal data and structure refinement parameters for 1 and 2.

	1	2
Empirical formula	C _{25,50} H ₂₂ Cl ₂ FeN ₂ Ru	C29H29ClFeN2Ru
Crystal system	Monoclinic	Tetragonal
Space group	C2/c	I4 ₁ cd
a (Å)	19.5782(16)	21.997(8)
b (Å)	10.6832(5)	21.997(8)
c (Å)	22.3147(14)	21.293(4)
α (deg)	90.00	90.00
β (deg)	108.426(8)	90.00
γ (deg)	90.00	90.00
$V(Å^3), Z$	4428.0(5), 8	10303(6), 16
λ (Å)	0.71073	0.71073
Color and habit	Black, blocks	Black, blocks
T (K)	150(2)	293(2)
Reflns collected(R_{int})	15905 (0.0260)	43730(0.1738)
Reflns/restraint/params	3907/0/285	5820/1/311
D_{calcd} (Mg m ⁻³)	1.753	1.666
$\mu ({\rm mm}^{-1})$	1.596	1.280
GOF on F^2	1.029	0.994
Final <i>R</i> indices $I > 2\sigma(I)$	R1 = 0.0272	R1 = 0.0560
	wR2 = 0.0685	wR2 = 0.1294
R indices(all data)	R1 = 0.0685	R1 = 0.0828
. ,	wR2 = 0.0704	wR2 = 0.1505

removed under reduced pressure and residue extracted with dichloromethane (5 mL) and filtered. Addition of an excess of hexane to the filtrate afforded yellow colored product which was separated by filtration, washed with diethyl ether and dried under vacuum. Yield: 0.165 g, 68%. Anal. Calc. for C₄₈H₄₄N₂SF₃O₃PFeRu: C, 59.20; H, 4.55; N, 2.88%. Found: C, 59.34; H, 4.62; N, 2.70%. IR (KBr pellets, cm⁻¹): 473, 517, 568, 667, 720, 770, 812, 893, 990, 1032, 1156, 1205, 1249, 1340, 1391, 1460, 1537, 1558, 2922, 3093. ¹H NMR (δ ppm): 1.02 (d, 6H, *J* = 6.6 Hz), 1.70 (s, 3H), 2.17 (m, 1H), 4.09 (s, 5H), 4.47 (s, 2H), 4.57 (s, 2H), 5.82 (d, 2H, *J* = 6.0 Hz), 5.92 (d, 2H, *J* = 6.6 Hz), 6.29 (d, 2H, *J* = 3.9 Hz), 7.36–7.47 (m, 17H), 7.62 (s, 2H). UV–vis. (CH₂Cl₂, λ_{max} nm, ϵ M⁻¹ cm⁻¹): 504 (3.14 × 10⁴), 436 (1.07 × 10⁴), 350 (1.74 × 10⁴), 241 (5.30 × 10⁴).

2.3. X-ray crystallography

Crystals suitable for single crystal X-ray diffraction analyses were obtained by slow diffusion of hexane to a dichloromethane solution of **1** and **2**. Intensity data were collected on a OXFORD DIFFRACTION × CALIBUR-S diffractometer equipped with graphite Mo K α radiation ($\lambda = 0.71073$ Å) at 293(2) K. The structures were solved by direct methods (SHELXS 97) and refined by full-matrix least squares procedure based on F^2 (SHELX 97) [26]. All the non hydrogen atoms were refined anisotropically and hydrogen atoms located at calculated positions and refined using a riding model with isotropic thermal parameters fixed at 1.2 times the U_{eq} value of the appropriate carrier atom.

3. Results and discussion

3.1. Syntheses and characterization

The ligand 5-ferrocenyldipyrromethane was synthesized by reaction of ferrocenyl-carboxaldehyde with an excess of pyrrole following the literature procedure [25]. The dimeric chloro bridged arene ruthenium complexes [{(η^6 -arene)Ru(μ -Cl)Cl}₂] (η^6 -arene = C₆H₆, C₁₀H₁₄) reacted with fcdpm obtained *in-situ* by oxidation of 5-ferrocenyldipyrromethane with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in a mixture of CH₂Cl₂/CH₃OH (1:1, v/v) at r.t. to afford heteroleptic dipyrrinato complexes [(η^6 -arene)RuCl(fcdpm)] (η^6 -arene = C₆H₆, **1**;C₁₀H₁₄, **2**). The rhodium and iridium complexes, [(η^5 -C₅Me₅)MCl(fcdpm)] [M = Rh(III) **3**, Ir(III) **4**] were synthesized in an analogous manner from the reactions of [{(η^5 -C₅Me₅)M(μ -Cl)Cl}₂] [M = Rh (III), Ir(III)] with fcdpm. A simple scheme showing synthesis of the complexes is depicted in Scheme 1.

Further, the complex $[(\eta^6-C_{10}H_{14})RuCl(fcdpm)]$ (2) reacted with NCS⁻ and PPh₃ in dry acetone to yield substitutional products (Scheme 2). Its reaction with NH₄SCN under stirring condition gave 5, while synthesis of **6** was achieved by abstraction of Cl⁻ using AgSO₃CF₃ followed by addition of PPh₃.

Table 2Selected bond length and angles for 1 and 2.

1		2	
Ru(1)-N(1)	2.0628	Ru(1)-N(1)	2.0817
Ru(1)-N(2)	2.0715	Ru(1)–N(2)	2.0736
Ru(1)–Cg	1.6738	Ru(1)–Cg	1.6932
$Ru(1)-C_{av}$	2.182	$Ru(1)-C_{av}$	2.210
Ru(1)-Cl(1)	2.4134	Ru(1)-Cl(1)	2.4204
Cg-Ru(1)-Cl(1)	126.87	Cg-Ru(1)-Cl(1)	128.94
Cg-Ru(1)-N(1)	127.71	Cg-Ru(1)-N(1)	128.43
Cg-Ru(1)-N(2)	128.28	Cg-Ru(1)-N(2)	128.79
N(1)-Ru(1)-Cl(1)	88.72	N(1)-Ru(1)-Cl(1)	85.67
N(2)-Ru(1)-Cl(1)	87.24	N(2)-Ru(1)-Cl(1)	84.92
N(1)-Ru(1)-N(2)	83.87	N(1)-Ru(1)-N(2)	84.44



Fig. 2. ORTEP diagram of 1 at 30% thermal ellipsoid probability (H-atoms omitted for clarity).

All the complexes are air-stable, non-hygroscopic, orange red crystalline solids, soluble in common organic solvents like methanol, ethanol, acetone, dichloromethane, chloroform, dimethylformamide, dimethylsulfoxide and insoluble in diethyl ether petroleum ether and hexane. The complexes under investigation have been characterized by elemental analyses, spectral (IR, ¹H NMR, UV–vis) studies and structures of **1** and **2** have been authenticated crystallographically.

IR spectra of the complexes displayed a peak at ~1556 cm⁻¹ assignable to ν (C=N_{pyr}) pyrrolic ring vibrations. In addition, complex **5** displayed a new peak at 2100 cm⁻¹ attributable to C–N stretching of the SCN⁻ ligand. Vibrations due to the counter anion SO₃CF₃⁻ appeared as a strong band at 1156 cm⁻¹ in the IR spectrum of **6** [8,9].

¹H NMR spectral data of the compounds along with their assignments are summarized in experimental section. In general, ¹H

NMR spectra of the complexes displayed three sets of Cp protons associated with fcdpm at ~4.17, 4.47 and 4.76 ppm. The pyrrolic protons resonated at ~6.49 (d, 2H), 7.66 (d, 2H), 8.01 (s, 2H) ppm (please see experimental section). Both the *Cp* and pyrrolic protons exhibited downfield shift in comparison to uncordinated fcdpm. The shift in position of various signals may be attributed to the linkage of fcdpm to respective metal centres through nitrogen donor sites in monoanionic chelating fashion. Further, the signals associated with hydrocarbon ligands η^6 -C₆H₆, η^6 -C₁₀H₁₄ and η^5 -C₅Me₅ exhibited insignificant shift and resonated at their usual positions [21-24]. An analysis of overall data suggested that the reasonances corresponding to various protons of fcdpm and arene protons displayed an inappreciable shift indicating week interaction between fcdpm and metal centres. The position and integrated intensity of various resonances corroborated well to a system involving coordination of fcdpm to the respective metal centres.



Fig. 3. ORTEP diagram of 2 at 30% thermal ellipsoid probability (H-atoms omitted for clarity).

X–H–Cg	H…Cg (Å)	H-(ring plane) (Å)	C-Cg (Å)	C–H–Cg (deg)	γ (deg)
Complex 2 $C(4)-H(4)Cg(C25C26C27C28C29)^{a}$ $C(10)-H(10A)Cg(N2C16C17C18C19)^{b}$ a = -X, -Y, Z; b = X,Y,Z.	2.72 2.65	2.629 2.551	3.4822 3.5824	135 164	15.01 15.64
Complex 1 Cg(C16C17C18C19C20)–Cg(C21C22C23C24C25) ^a		Cg–Cg 3.2785	α (deg) 5.32	β (deg) 2.94	γ (deg) 2.55
Complex 2 Cg(C20C21C22C23C24)-Cg(C25C26C27C28C29) ^b a = X,Y,Z; b = X,Y,Z. D-H···A	3.3120 D(D-H)	4.92 d(H…A)	3.02 d(D···A	1.94 ∟(DHA)	
Complex 2 (Å and °) C(22)-H(22)Cl(1) ^b a = -1/2 + x, 1/2 - y.z.	0.95	2.53	3.3903	151	



Fig. 4. Zig-zag structural motif in 2 resulting from C-H...Cl interactions.

The electronic absorption spectra of **1–6** were acquired in dichloromethane and resulting spectra for **1–4** is depicted in Fig. 1. All the complexes under investigation displayed intense bands ($\epsilon > 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) between 200 and 400 nm assignable to $\pi - \pi^*$ transitions of dipyrrin and arene. The intense low energy absorption bands extending between 400 and 540 nm have been assigned to highly conjugated dipyrrin based $\pi \to \pi^*$ transitions [5,6,13].

Molecular structures of 1 and 2 have been determined crystallographically. Details about the data collection, solution and refinement are summarized in Table 1 and selected geometrical parameters are given in Table 2. ORTEP views at 30% thermal ellipsoid probability are depicted in Figs. 2 and 3. Overall arrangement of the various ligands about metal centre ruthenium in 1 and 2 are analogous and adopted typical "piano-stool" geometry. The coordination sites about ruthenium centre in both the complexes are occupied by two pyrrolic nitrogen atoms from fcdpm, the chlorogroup and arene ring coordinated in η^6 -manner (benzene, **1**: p-cymene, **2**). The Ru–N and Ru–Cl bond distances [Ru-N1 = 2.0628 Å, Ru-N2 = 2.0715 Å, Ru-Cl1 = 2.4134 Å in 1;Ru-N1 = 2.0817 Å, Ru-N2 = 2.0736 Å, Ru-Cl1 = 2.4204 Å in **2**] are normal and comparable to those in other related systems [8,9]. The N-Ru-N and N-Ru-Cl angles are less than 90° [N1-Ru-N2 = 83.87°, N1-Ru-Cl1 = 88.72°, N2-Ru-Cl1 = 87.24° in 1; $N1-Ru-Cl2 = 84.44^{\circ}$, $N1-Ru-Cl1 = 89.4^{\circ}$, $N2-Ru-Cl1 = 85.67^{\circ}$ in 2] and consistent with the "piano stool" arrangement of various groups about the metal centre [Table 2] [8,9]. The average Ru–C bond distances in 1 and 2 are 2.182 [range 2.157–2.202 Å] and 2.210 Å [range 2.186–2.223 Å], respectively. The centroid of η^6 -C₆H₆ and η^6 -C₁₀H₁₄ rings is separated from metal centre ruthenium by 1.6738(1) and 1.6932(2) Å. These are close to the values reported in other $(\eta^6 - C_6 H_6) Ru(II)$ and $(\eta^6 - C_{10} H_{14}) Ru(II)$ complexes [8,9]. Matrices for weak bonding interactions in **1** and **2** are gathered in Table 3. Crystal structure of 2 revealed the presence of extensive inter-molecular C-H...Cl interactions. These interactions lead to creation of zig-zag structural motif shown in Fig. 4. The C-H...Cl distances are 2.53 Å, which are less than the sum of van der-Waals radii and within the reported range [27].

4. Conclusions

Through this work we have presented the synthesis, spectral and structural characterization of mononuclear complexes containing (η^6 -arene)Ru-, (η^5 -C₅Me₅)Rh- and (η^5 -C₅Me₅)Ir- moieties and 5-ferrocenyldipyrromethene for the first time. Reactivity of the representative complex [(η^6 -C₁₀H₁₄)RuCl(fcdpm)] have also been examined with NH₄SCN, and PPh₃ to afford substutional derivatives. Single crystal X-ray diffraction analyses on [(η^6 -C₆H₆)RuCl(fcdpm)] and [(η^6 -C₁₀H₁₄)RuCl(fcdpm)] revealed the coordination of ligand fcdpm with the metal centres in a chelating mode as an anionic ligand.

Acknowledgment

Thanks are due to the Council of Scientific and Industrial Research, New Delhi, India for providing financial assistance to through the scheme [HRDG 01(2074)/06/EMR-II]. M.Y. acknowl-edges CSIR for awarding SRF 9/13(312)/2010-EMR-I. We are also thankful to the Head, Department of Chemistry, Banaras Hindu University, Varanasi (U.P.), India for extending laboratory facilities and Prof. P. Mathur, Indian Institute of Technology, Powai, Mumbai, for providing single crystal X-ray data.

Appendix. Supplementary material

CCDC-779162 for **1** and 779163 for **2** contains the supplementary crystallographic data for this paper. This data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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