Synthesis, Spectroscopic and Molecular Studies of Half-Sandwich η⁶-Arene Ruthenium, Cp* Rhodium and Cp* Iridium Metal Complexes with Bidentate Ligands

Mahesh Kalidasan,^[a] R. Nagarajaprakash,^[b] Scott Forbes,^[c] Yurij Mozharivskyj,^[c] and Kollipara Mohan Rao^{*[a]}

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Abstract. The bidentate ligand benzoyl(2-pyridyl)thiourea (**L1**) was prepared by reaction of benzoyl isothiocyanate with primary amine (2-aminopyridine) but the reaction with secondary amine bis(2-pyridyl)amine, yielded the unexpected product bis(2-pyridyl)benzoylamine (**L2**). Mononuclear complexes of the general formula [(η^6 -arene)Ru(L)Cl]⁺ {where, L = L1, arene = benzene (1); *p*-cymene (2); L = L2, arene = benzene (5); *p*-cymene (6)} and [Cp**M*(L)Cl]⁺ {where, L = L1, *M* = Rh (3), Ir (4); L = L2, *M* = Rh (7), Ir (8)},

Introduction

The study of half-sandwich arene Ru, Cp*Rh and Cp*Ir complexes is a versatile subject in organometallic chemistry due to their unique properties viz. mild reaction conditions required for synthesis, as well as their high yield, stability and solubility under aqueous conditions.^[1–3] It has been shown that the nature of the arene, the chelating ligands, and the leaving group in these complexes strongly influence their chemical and biological activity.^[4,5] The source of metals for all these halfsandwich complexes are starting dimers, like $[(\eta^6-benzene/p$ cymene)RuCl₂]₂ and $[Cp*M(\mu-Cl)Cl]_2$ (M = Rh, Ir), which undergo a rich variety of chemistry via intermediate chloro bridge cleavage reaction, leading to the formation of a series of neutral and cationic mononuclear complexes.^[6-9] Recently, these complexes have been used catalyst in various organic transformation reactions^[10–15] and attracted considerable interest as a potential anticancer agent because of their low toxicity, often good aqueous solubility and their efficacy against platinum drug resistant tumors.^[16–19] Among various bidentate ligands, 2,2'-dipyridylamine (dpa) derivatives and N-substituted pyridine-2-thiourea based ligands have shown interest in various

*	Prof. Dr. K. M. Rao
	Fax: +91-364-2550076
	E-Mail: mohanrao59@gmail.com
[a]	Department of Chemistry
	North Eastern Hill University
	CI 'II 702.020 T I'

- Shillong 793 022, India[b] Department of Chemistry Pondicherry University Puducherry 605014, India
- [c] Department of Chemistry and Chemical Biology McMaster University Hamilton, ON L8S 4M1, Canada

respectively, were formed by reaction of the ligands L1 and L2 with precursor complexes $[(\eta^6\text{-}arene)Ru(\mu\text{-}Cl)Cl]_2$ and $[Cp^*M(\mu\text{-}Cl)Cl]_2$ (M = Rh, Ir). The cationic complexes were characterized by FT-IR, UV/Vis, and ¹H-NMR spectroscopy as well as mass spectrometry. X-ray crystallographic studies of these complexes reveal piano-stool-like arrangements around the metal atoms with six-membered metallacycles in which L1 and L2 act as a N,S- and N,N' chelating ligands, respectively.

fields and their metal complexes have been utilized for several decades and are widely employed in coordination chemistry, supramolecular chemistry and materials synthesis.^[20–25] To the best of our knowledge there is no report available in the literature regarding reactions of arene ruthenium and Cp*Rh and Cp*Ir complexes with benzoyl-(2-pyridyl)thiourea/ bis(2-pyridyl)benzoylamine ligands. Herein, the syntheses of a series of new mononuclear half-sandwich complexes of arene Ru^{II}, Cp*Rh^{III} and Cp*Ir^{IIII} with these bidentate ligands are reported. The ligands used in this study are shown in Scheme 1.



Scheme 1. Ligands used in this study.

Results and Discussion

Syntheses

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Benzoyl(2-pyridyl)thiourea (L1) is synthesized by reaction of benzoyl isothiocyanate with 2-aminopyridine in anhydrous acetone. Similarly, we tried to isolate benzoyl-N,N'-bis(2-pyridyl)thiourea, by reacting a secondary amine such as 2,2-dipyridylamine to benzoyl isothiocyanate, but we isolate unexpected product N-bis(2-pyridyl)benzoylamine (L2) in quantitative yield and this conversion is unambiguous.^[26] The reaction of $[(\eta^{6}-\text{arene})\text{Ru}(\mu-\text{Cl})\text{Cl}]_{2}$ (arene = benzene and *p*-cymene) and $[Cp*M(\mu-Cl)Cl]_2$ (M = Rh, Ir) with 1:2 molar equivalents of ligand benzoyl(2-pyridyl)thiourea yielded mononuclear complexes $[(\eta^6\text{-}arene)Ru(N\cap S)Cl]PF_6$ and $[Cp^*M(N\cap S)Cl]PF_6$ (Scheme 2). In the case of bis(2-pyridyl) benzoylamine and NH_4PF_6 yield complexes of the type [(η^6 arene)Ru(N \cap N)Cl]PF₆ and [Cp*M(N \cap N)Cl]PF₆ in methanol (Scheme 3) with same precursor complexes. These complexes are isolated in very good yield and purified by recrystallization method. Some of complexes are isolated with a chloride as counterion, which improve the solubility in aqueous solvent compare to PF₆ anion but these complexes are less stability rather than of PF₆ anion complexes. All these complexes are yellow-orange crystalline solids, resulting as non-hygroscopic, air-stable. They are highly soluble in acetone, acetonitrile and DMSO but they are sparingly soluble in methanol, dichloromethane and chloroform. The complexes were fully characterized by IR, ¹H NMR, and electronic spectroscopy as well as mass spectrometry.



Scheme 2. Preparation of metal complexes with ligand L1.



Scheme 3. Preparation of metal complexes with ligand L2.

IR Spectroscopy

IR spectra of metal complexes of ligand L1 exhibit vibration frequency bands at 1313 cm⁻¹ and 1220 cm⁻¹ for the C=S vibration whereas the free ligand shows these bands at 1340 cm⁻¹ and 1250 cm⁻¹. This observation indicate that metal is coordinated through sulfur and nitrogen. The complexes also display stretching frequency bands at 1670 cm⁻¹ for C=O group and 1570 cm⁻¹, 1434 cm⁻¹ for C=C and C=N bonds.^[23b] The IR spectrum of the free ligand L2, shows C=O stretching frequency at 1660 cm⁻¹, sharp bands at 1584 cm⁻¹ and

1434 cm⁻¹ which is corresponding to the stretching frequencies of C=C and C=N bonds respectively. IR spectra of metal complexes with ligand L2 have displayed similar pattern of free ligand, C=O stretching frequency absorption at around 1690 cm⁻¹ and stretching frequency of C=C and C=N have shown sharp bands at 1601 cm⁻¹ and 1468 cm⁻¹ respectively. Upon coordination to metal atoms, the IR stretching frequency of these groups is shifted to higher frequency region.^[27] In addition, these complexes display very sharp bands at 841 cm⁻¹ and 558 cm⁻¹ that are corresponding to P-F stretching frequency of counterion.^[28]

¹H NMR Spectroscopy

The ¹H NMR spectrum of the free ligand L1 shows three resonances for the protons of the phenyl ring at 7.11 to 7.7 ppm and four signals for the protons of the 2-pyridyl ring are observed at 7.85 to 8.90 ppm, while the NH proton resonances are observed at $\delta = 9.11$ and 8.37 ppm as singlet signals. In the metal complexes, the NH resonances are observed low field at $\delta = 14.25$ ppm and 12.70 ppm and the other signals are shown as similar pattern of free ligand except the signals are shifted to downfield. The ligand L2 displays three doublets and four triplets in the range 8.34 to 7.01 ppm that are assigned to pyridyl and phenyl rings respectively. Upon coordination with the metal atom, each metal complex has shown seven signals in the range around 9.00 to 7.30 ppm similar to free ligand, which is, indicated that formation of mononuclear complexes. For all these complexes, the signals of the coordinated dipyridyl and phenyl protons are shifted to considerable downfield as compared to free ligand due to consequence of their coordination to metal atoms.^[29] Besides these signals, complexes 1 and 5 exhibit a singlet signal at $\delta = 6.35$ ppm for the protons of the benzene ligand. Complexes 2 and 6 exhibit two doublet signals at $\delta = 6.30$ ppm and 6.02 ppm, which correspond to the aromatic *p*-cymene ring CH protons, a septet at δ = 3.04 ppm as well as a doublet observed at δ = 1.35 ppm for the protons of isopropyl group and a singlet at $\delta = 2.04$ ppm for the methyl proton of *p*-cymene ligand, which are shifted downfield compared to similar complexes. The Cp*Rh complexes 3 and 7 and the Cp*Ir complexes 4 and 8 display singlet signals at $\delta = 1.75$ and 1.76 ppm due to the Cp* ligand, which are shifted slightly downfield compared to the starting materials.^[7]

Mass Spectrometry

Mass spectrometric studies were carried out for all newly synthesized complexes. Parent peaks could be found in ESI spectra at (m/z) 473.14 (1), 529.15 (2), 532.10 (3) 621.21 (4), 490.11 (5), 546.16 (6), 548.20 (7) and 638.24 (8). The mass spectra showed prominent peaks corresponding to the loss of the thiocarboamide ion in complexes 1–4 and the benzoyl group in complexes 5–8 from molecular ion peaks, but loss of arene group is not observed which indicate that the stronger bond with metal ions to these groups. Mass spectra values are strongly support the formation of mononuclear complexes.

Molecular Structures

The molecular structure of mononuclear complexes has been established by single-crystal X-ray structure analysis. ORTEP diagrams of the complexes including atom-numbering scheme are shown in Figure 1, Figure 2, Figure 3, Figure 4, Figure 5, Figure 6, and Figure 7. Crystallographic and structure refinement parameters for complexes have shown in Table 1. Se-



Figure 1. ORTEP diagram of complex $[(\eta^6-p-cymene)RuCl(L1)]Cl(2)$ with 50% probability thermal ellipsoids. Hydrogen atoms and counter anion are omitted for clarity.



Figure 2. ORTEP diagram of complex [Cp*RhCl(L1)]Cl (3) with 50% probability thermal ellipsoids. Hydrogen atoms and counter anion are omitted for clarity.



Figure 3. ORTEP diagram of complex [Cp*IrCl(L1)]Cl (4) with 50% probability thermal ellipsoids. Hydrogen atoms, solvent molecules and counter anion are omitted for clarity.



Figure 4. ORTEP diagram of complex $[(\eta^6\text{-benzene})\text{RuCl}(\text{L2})]\text{PF}_6(5)$ with 50% probability thermal ellipsoids. Hydrogen atoms and counter anion are omitted for clarity.



Figure 5. ORTEP diagram of complex $[(\eta^6-p\text{-}cymene)RuCl(L2)]PF_6$ (6) with 50% probability thermal ellipsoids. Hydrogen atoms and counter anion are omitted for clarity.



Figure 6. ORTEP diagram of complex $[Cp*RhCl(L2)]PF_6$ (7) with 50% probability thermal ellipsoids. Hydrogen atoms and counter anion are omitted for clarity.



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Figure 7. ORTEP diagram of complex [Cp*IrCl(L2)]PF₆ (8) with 50 % probability thermal ellipsoids. Hydrogen atoms and counter anion are omitted for clarity.

lected bond lengths and bond angles are shown in Table 2 and the N-H···Cl bonding interactions are shown in Table 3. Complexes 2 and 6 crystallize in the monoclinic space group $P2_1/c$; complexes 3 and 4 crystallize in the orthorhombic space group *Pbca* and complexes 5, 7, and 8 crystallized in the tri-

clinic space group $P\bar{1}$, respectively. All complexes exhibit a three-legged piano stool geometry with the metal atom coordinated by the arene/Cp* ligand in the chelating k^2 -N,S mode/N,N' mode and a chloride ligand. The chloride anion acts as counterion in complexes **2–4**, and the PF₆ anion acts as counterion in complexes **5–8**, respectively. The metal atoms in all complexes adopt a pseudo-octahedral arrangement and the ligand is found to coordinate in the bidentate mode to generate a six-membered metallacycle.

X-ray crystallography studies of all complexes show slightly different bond lengths and angles between N.S- and N.N'-coordinate complexes. In complexes 2, 3, and 4, only the N,S-coordination mode like N-substituted 2-pyridine-carbothioamide complexes but in contrast to organometallic Nphenyl-picoliamide complexes where amide switching is detected, probably due to increased stability of the metal to sulfur bond, as suggested by the HSAB principle.^[24] The Ru-S bond length in complex 2 is 2.360(13) Å, slightly longer than the other Rh/Ir complexes (2.3386(14) (3), 2.3479(17) Å (4)) but smaller than reported value $[(\eta^6-arene)Ru(NS)Cl]^+$ (2.3815– 2.3742 Å)^[30] and both are within the range of the reported Ru-S bond lengths (2.354–2.415 Å).^[31,32] Complexes 5–8 have shown that metal bonded through both pyridine nitrogen donor sites with bond lengths in the range 2.096–2.128 Å. The M–Cl bonds are almost equivalent to 2.400 Å which are closely re-

Table 1. Crystallographic and structure refinement parameters for complexes.

	[2] •Cl	[3]•Cl	[4]•Cl•2H ₂ O	[5]•PF ₆ •Hexane	[6]•PF ₆	[7]•Acetone
Chemical formula	C23H25Cl2N3ORuS	C23H26Cl2N3ORhS	C23H28Cl2N3O2IrS	C23H19ClF16N3OPRu1	C27H27ClF6N3OPRu	C27H28ClF6N3OPRh
Formula Mass	563.49	566.35	691.66	634.90	691.00	693.85
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Triclinic	Monoclinic	Triclinic
a /Å	11.8013(4)	16.566(5)	16.5671(5)	8.5615(17)	20.5310(6)	8.1424(16)
b /Å	11.6159(3)	15.216(5)	15.1811(5)	12.165(2)	15.9530(3)	8.5413(17)
c /Å	17.7498(5)	20.736(6)	20.8675(6)	13.108(3)	17.4631(4)	21.543(4)
a /°	90	90	90	93.59(3)	90.00	88.94(3)
β /°	92.675(2)	90	90	92.75(3)	99.591(2)	88.85(3)
γ /°	90	90	90	91.54(3)	90.00	86.62(3)
Unit cell volume /Å3	2430.54(12)	5226.6(18)	5248.3(3)	1360.4(5)	5639.8(2)	1495.1(5)
Temperature /K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Space group	P21/c	Pbca	Pbca	ΡĪ	P21/c	ΡĪ
Z	4	16	8	2	8	2
Index ranges	$-6 \le h \ge 15$	$-15 \le h \ge 20$	$-11 \le h \ge 22$	$-10 \le h \ge 10$	$-25 \le h \ge 24$	$-9 \le h \ge 9$
	$-14 \le k \ge 14$	$-19 \le k \ge 12$	$-20 \le k \ge 15$	$-14 \le k \ge 14$	$-19 \le k \ge 19$	$-7 \le k \ge 11$
	$-23 \le l \ge 23$	$-25 \le l \ge 13$	$-26 \le l \ge 24$	$-15 \le l \ge 15$	$-21 \le l \ge 21$	$-28 \le l \ge 28$
D_c /g·cm ⁻³	1.540	1.439	1.751	1.550	1.628	1.541
μ /mm ⁻¹	0.971	0.957	5.400	0.795	0.774	0.777
F(000)	1144	2304	2832	632	2784	700
θ Range	28.77, 3.42	26.37, 3.15	28.732, 3.109	24.86, 1.56	26.37, 3.34	24.35, 1.90
Reflections collected	10668	16449	17866	30689	30385	28017
Independent reflections	5517	5324	6100	4693	9167	5170
	[R(int) = 0.0167]	[R(int) = 0.0229]	[R(int) = 0.0277]	[R(int) = 0.0292]	[R(int) = 0.0337]	[R(int) = 0.0337]
Completeness to $\theta = 25.00^{\circ}$	99.7	99.8	99.8	99.6	99.8	99.2
Data/restraints/parameters	5517/0/290	5324/1/306	6100/0/302	4693/0/325	11502/0/728	5170/0/369
Goodness-of-fit on F^2	1.084	1.115	1.052	0.976	1.045	1.156
Final R indices	$0.0273, wR_2 =$	$0.0570, wR_2 =$	$0.0321, wR_2 =$	$0.0385, wR_2 = 0.0999$	$0.0432, wR_2 =$	$0.0464, wR_2 =$
$[I > 2\sigma (I)]^*$	0.0672	0.1903	0.0643		0.1052	0.1255
R indices (all data)	$0.0354, wR_2 = 0.0638$	$0.0694, wR_2 = 0.2036$	$0.0546, wR_2 = 0.0734$	$0.0515, wR_2 = 0.1037$	$0.0609, wR_2 = 0.1178$	$0.0562, wR_2 = 0.1286$
Max, Min $\Delta \rho$ /e·Å ⁻³	0.522, -0.065	1.516, -0.574	1.069, -0.741	0.923, -0.430	1.000, -1.006	0.888, -0.594

* Structures were refined on F_0^2 : $wR_2 = [\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma w(F_0^2)^2]^{1/2}$, where $w^{-1} = [\Sigma(F_0^2) + (aP)^2 + bP]$ and $P = [\max(F_0^2, 0) + 2F_c^2]/3$.

Complex	2	3	4	5	6	7	8
M(1)-S(1)	2.360(13)	2.3386(14)	2.3479(17)				
M(1) - N(1)	2.117(4)	2.088(4)	2.099(5)	2.096(3)	2.128(3)	2.122(4)	2.122(13)
M(1) - N(3)				2.100(3)	2.125(3)	2.124(4)	2.112(13)
M(1) - Cl(1)	2.409(13)	2.3863(17)	2.3479(17)	2.391(12)	2.397(9)	2.392(15)	2.391(4)
$M(1)-C_{ave}$	2.204(5)	2.160(6)	2.164(7)	2.193(5)	2.193(5)	2.153(5)	2.164(15)
M(1)-CNT	1.697	1.793	1.796	1.682	1.692	1.778	1.790
N(1) - M(1) - S(1)	89.01(11)	87.18(14)	87.26(15)				
S(1) - M(1) - Cl(1)	86.86(5)	89.06(6)	87.93(7)				
N(1) - M(1) - N(3)				85.42(11)	83.22(11)	85.08(06)	84.7(5)
N(1) - M(1) - Cl(1)	85.62(11)	87.82(14)	87.26(15)	83.16(9)	83.97(8)	86.42(13)	84.8(4)
N(3) - M(1) - Cl(1)				84.81(9)	85.32(9)	86.62(12)	85.5(4)

Table 2. Selected bond lengths /Å and angles /°.

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CNT represents the centroid of the arene/Cp* ring; Cave represents the average bond length centroid of the arene/Cp* ring carbon and metal atom.

Table 3. N–H…Cl bonding	g interactions in	n complexes 2–4.
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Complex	Donor-H···Acceptor	D–H	Н•••А	D•••A	D–H•••A
2	N(2)–H(2)•••Cl(2)i	0.62(5)	2.59(5)	3.173(6)	157(7)
	N(3)-H(3)-Cl(2)i	0.65(7)	2.50(7)	3.087(5)	152(8)
3	N(2)-H(2)-Cl(2)	0.86	2.23	3.0650(6)	163
	N(3)-H(3)-Cl(2)	0.86	2.64	3.3751(7)	145
4	N(2) - H(2) - Cl(2)	0.65(8)	2.77(7)	3.373(7)	154(7)
	N(3)–H(3)•••Cl(2)	0.84(8)	2.26(8)	3.071(7)	164(7)

Symmetry transformations used to generate equivalent atoms: i = 1-x, -1/2+y, 1/2-z.

lated to previous reported half-sandwich arene ruthenium complexes with bis(2-pyridyl)benzoylamine,^[33] 3-(di-2-pyridylaminomethyl) benzamide,^[34] and similar systems of $[Cp*Ir(N \cap N)Cl]^+$ where, $N \cap N$ is bis(2-pyridyl) benzylamine, 3-(di-2-pyridylaminomethyl)benzamide ligand^[33-35] and other dipyridylamine based ligand.^[34] The bite angle of metal with ligand is around 85° which are normal and consistent with k^2 coordination of ligand. The bond angle of metal with ligand and chloride atom is also similar to bite angle that is nearly 90° and is evidence for "piano stool" geometry.

Crystal structure analyses of the metal complexes have revealed the presence of extensive inter-/intramolecular C-H/X(O, Cl and F) and C–H/ π interactions, as well as π ··· π interactions. These types of interaction play significant role in the building of huge supra-molecular motifs and dominant role in stabilizing the stacking of molecules.^[36,37] Weak interactions like S…O, C–H/Cl and C–H/ π interactions, or π … π interactions were observed in the solid state packing of the complexes. Analyses of complexes 2-4 revealed five-membered intramolecular O···S interactions with bond lengths 2.886, 2.849, and 2.824 Å, respectively. But these O····S interactions differ from the free ligand of benzoyl(2-pyridyl)thiourea, which shows five-membered intramolecular N-H···O hydrogen bonding interaction. The counterion of chloride atom in the complexes involves with thiourea unit in the formation of the resulting intermolecular N-H···Cl hydrogen-bonded network and N-H···Cl hydrogen bonding have shown in Table 3. The N-H···Cl contact typically has a separation of 3.375-3.065 Å, the H···Cl distances are in the range 2.23-2.77 Å, and the N-H···Cl angles are in the range 145-164°, which is in the general range of strong N-H···Cl bonds.^[23]

Complex 5 form dimers via CH/Cl and weak CH/Cl and CH/O intermolecular interactions with bond lengths 2.855, 2.866, and 2.511 Å by adopting dimeric units of $R_2^2(8)$, $R_{2}^{2}(14)$, $R_{3}^{2}(6)$ respectively which are stabilized by crystal packing (Figure 8). Additionally, there is an interaction of the pyridyl rings (C12/C13/C14/C15) in the molecule by $\pi \cdots \pi$ interactions with the neighboring pyridyl molecule (C12/C13/ C14/C15) with a bond length of 3.307 Å.^[38]. Furthermore this complex has shown a mutual intermolecular C-H/Cl and C- H/π bonding network resulting in the formation of a 2D sheetlike arrangement consisting of various dimeric units. Some interesting supramolecular interactions like C-H/Cl and C-H/ π interactions are observed in the solid state packing of com-



Figure 8. Portions of the packing diagram of complex 5 (a). C-H···Cl interaction; (b). C–H···Cl and π ··· π interaction; (c). C–H···O interaction along c axis.



Figure 9. Portions of packing diagram of showing C-H···Cl and C-H··· π interaction along b axis in (a) Complex 7, b) Complex 8.



Figure 10. UV/Vis spectra of all complexes in the range 200-650 nm.

plexes 7 and 8 (Figure 9). Unlikely, complexes 7 and 8 form similar kinds of two-dimensional networks via C–H/Cl and C– H/ π short contacts. Two molecules interact via C–H/ π short contacts to form a dimeric pair and this dimeric pair is linked via mutual C–H/Cl short contacts to form a 2D sheet along *b* axis with bond lengths 2.827 and 2.886 Å (7), and 2.849 and 2.760 Å (8), respectively. Complex 8 shows an interesting arrangement in crystal packing of one PF₆ anion molecule occupy into cavity of chain which is two-dimensional networks via C–H/Cl and C–H/ π short contacts. All the interactions are intermolecular in nature and the short contact distances are comparable to the literature reports.^[39–41]

UV/Vis Spectroscopy

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UV/Vis spectra of complexes are recorded in acetonitrile at approx. 10^{-4} M concentration in the range 200–800 nm and the spectra of all complexes are shown in Figure 10. The UV/Vis spectra of complexes exhibit intense ligand-localized or intraligand π - π * transitions in the UV region and metal to ligand charge transfer (MLCT) of the $d\pi$ (M)– π *(L) band in the visible region.^[42] The UV/Vis spectra of all complexes show two bands in the region 446–230 nm. The high intense absorption bands at approximately 230–320 nm are assigned to π - π */n– π * transitions while the low intensity bands observed around 406–446 nm are assigned to the metal to ligand charge transfer

transition (MLCT) arising from the excitation of electrons from the metal t_{2g} level to the empty molecular orbitals derived from the π^* level of the ligands.

Conclusions

A new series of arene ruthenium and Cp*Rh and Cp*Ir complexes with benzoyl(2-pyridyl)thiourea (L1)/bis(2-pyridyl)benzoylamine (L2) ligands was synthesized. All complexes were obtained in high yield, were soluble in polar solvents, and remarkably stable in air. IR and ¹H NMR spectroscopic studies of the complexes strongly supported the formation of the products. X-ray crystallographic studies of the complexes established the coordination of the ligand to the metal atoms in bidentate mode. The binding mode of metal with ligands L1 is N \cap S mode while L2 N \cap N mode. The synthesis of dinuclear complexes with L1 by using other binding sites like NN' or NO was unsuccessful. Moreover, metal complexes have been found to form inter-/intramolecular interactions such as O–S as well as CH···Cl, CH···π, or π···π interactions.

Experimental Section

Materials and Methods

RuCl₃•nH₂O, RhCl₃•nH₂O, IrCl₃•nH₂O (Arora Matthey Limited), α -Phellandrene, Benzoylchloride (Merck) and 1,4-cyclohexadiene,



1,2,3,4,5-pentamethylcyclopentadiene, 2-aminopyridine, 2,2-dipyridylamine (Aldrich) were purchased and used as received. Solvents were purified and dried according to standard procedures.^[43] The experiments were performed under normal conditions. The starting precomplexes $[(\eta^6\text{-benzene})\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$, $[(\eta^6\text{-}p\text{-}$ cursor metal cymene)Ru(μ -Cl)Cl]₂^[44,45] and [Cp* $M(\mu$ -Cl)Cl]₂ (M = Rh, Ir)^[46] were prepared according to the literature methods. The ligand benzoyl-(2pyridyl) thiourea, bis(2-pyridyl)benzoylamine were prepared to modify the reported procedure.^[47] ¹H NMR spectra were recorded with a Bruker Avance II 400 MHz. Infrared spectra were recorded as KBr pellets with a Perkin- Elmer 983 spectrophotometer. Mass spectra were obtained from Water ZQ-4000 mass spectrometer by ESI method in positive mode. Elemental analyses were performed with a Perkin- Elmer-2400 CH/N analyzer. Absorption spectra were obtained at room temperature using a Perkin- Elmer Lambda 25 UV/Vis spectrophotometer.

Single-Crystal X-ray Structure Analyses

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The orange crystals of complexes 2-7 were obtained by slow diffusion of hexane into acetone solution and yellow crystals of complex 8 were obtained by slow evaporation of acetonitrile of the corresponding complex. Single crystal X-ray diffraction measurements were carried out on an Xcalibur, Eos, Gemini and STOE IPDSII diffractometer. Single crystals picked up from the samples were analyzed on a STOE IPDSII diffractometer using Mo Ka radiation in the whole reciprocal sphere. A numerical absorption correction was based on the crystal shape originally determined by optical face indexing but later optimized against equivalent reflections using the STOE X-Shape software.^[48] Crystal structures were determined and solved using the SHELX software.^[49] PLATON SQUEEZE was applied to the X-ray single crystal data to remove a highly disordered solvent which appeared to be "hexane" (5), "acetone" (7) and "acetonitrile" (8).^[50] The crystal structure of complex 8 could not be properly solved due to the residual electron densities are extremely high > 5.5; we have presented the data here to establish only the structure and composition of the molecule. In crystal structure of complex 2, chlorine atoms Cl2, Cl3 and Cl4 were refined with partial occupancy such that add up to 100%. Crystallographic details are summarized in Table 1 and selected bond lengths and bond angles and given in Table 2. Figure 1, Figure 2, Figure 3, Figure 4, Figure 5, Figure 6, and Figure 7 were drawn with ORTEP-3^[51] and Figure 8 and Figure 9 were drawn with MERCURY.

Syntheses of Metal Complexes 1-4

A mixture of the metal precursor $[(\eta^{6}\text{-arene})\text{Ru}(\mu\text{-Cl})\text{Cl}]_{2}$ or $[\text{Cp}^{*}M(\mu\text{-Cl})\text{Cl}]_{2}$ (0.1 mmol), benzoyl(2-pyridyl)thiourea (0.2 mmol) and 2.5 equivalents of NH₄PF₆ was dissolved in methanol (20 mL) and stirred at room temperature for 4 h. A yellow colored precipitate was formed upon evaporation of methanol solvent by rotary evaporator. The precipitate was washed with methanol and diethyl ether (3 × 10 mL) and dried in vacuo.

[(η^{6} -benzene)Ru(L1)Cl]PF₆ (1): Yield 85 mg (69%). IR (KBr (cm⁻¹)): v(NH) 3386 m, v(CH) 3056 m, v(C=O) 1699 s, v(C=C, C=N) 1598–1479 vs, v(C=S, C–N) 1313–1229 s, v_{bent}(CH) 773–706 m, v(P–F) 845, 555 s. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 14.33 (s, 1 H, NH), 12.81 (s, 1 H, NH), 8.72 (d, 1 H, *J*(H,H) = 5.25, py ring), 7.65 (d, *J*_{H,H} = 4.75 Hz, 1 H, py ring), 7.52 (d, *J*_{H,H} = 5.50 Hz, 2 H, ph ring), 7.50 (t, 1 H, py ring), 7.47 (t, 2 H, ph ring), 7.35 (t, 1 H, py ring), 7.11 (t, 1 H, ph ring), 6.32 (s, 6 H, benzene ring). ESI-MS: 473.14 [M⁺] peak, 436.20 [M⁺ − Cl] peak, 274.08 [(ben)Ru(2-py)⁺]

peak. **UV/Vis:** λ_{max} nm ($\epsilon / 10^{-4} \text{ m}^{-1} \text{ cm}^{-1}$): 255(0.49), 280(0.42), 392(0.04); **Elemental Anal.** for C₁₉H₁₇N₃OSRuClPF₆ (616.9): C 36.99 (calcd. 40.15); H 2.78 (2.95); N 6.81 (6.91).

[(η⁶-p-cymene)Ru(L1)Cl]PF₆ (2): Yield 97 mg (72%). IR (KBr (cm⁻¹)): v(NH) 3400 m, v(CH) 2963 m, v(C=O) 1714 s, v(C=C, C=N) 1600–1477 vs, v(C=S, C–N) 1312–1217 s, v_{bent}(CH) 780–709 m, v(P–F) 841, 554 s. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 14.35 (s, 1 H, NH), 12.82 (s, 1 H, NH), 8.75 (d, J_{H,H} = 5.50 Hz, 1 H, py ring), 7.70 (d, J_{H,H} = 4.75 Hz, 1 H, py ring), 7.53 (d, J_{H,H} = 5.25 Hz, 2 H, ph ring), 7.49 (t, 1 H, py ring), 7.46 (t, 2 H, ph ring), 7.34 (t, 1 H, py ring), 7.12 (t, 1 H, ph ring), 6.32 (d, J_{H,H} = 4.00 Hz, 2 H, ph ring), 6.12 (d, J_{H,H} = 4.00 Hz, 2 H, ph ring), 3.06 (sep, 1 H, Ar_(*p*-Cy)), 2.06 (s, 3 H, CH₃Ar_(*p*-Cy)), 1.37 (d, J_{H,H} = 4.50 Hz, 6 H, CH₃ Ar_(*p*-Cy)), 1.25 (d, J_{H,H} = 4.25 Hz, 6 H, CH₃Ar_(*p*-Cy)). ESI-MS: 529.15 [M⁺] peak, 492.12 [M⁺ – Cl] peak, 329.00 [(*p*-cy)Ru(2-py)⁺] peak. UV/Vis: λ_{max} nm (ε /10⁻⁴ M⁻¹ cm⁻¹): 257(0.46), 282(0.39), 403(0.03); Elemental Anal. for C₂₃H₂₅N₃OSRuClPF₆ (673.0): C 41.05 (calcd. 41.24); H 3.74 (3.87); N 6.24 (6.43).

[**Cp*Rh**(**L1**)**Cl**]**PF**₆ (3): Yield 92 mg (68%). IR (KBr (cm⁻¹)): v(NH) 3314 m, v(CH) 2970 m, v(C=O) 1706 s, v(C=C, C=N) 1598–1476 vs, v(C=S, C–N) 1318–1215 s, v_{bent}(CH) 782–712 m, v(P–F) 845, 554 s. ¹H **NMR** (400 MHz, CDCl₃, 25 °C): δ = 14.23 (s, 1 H, NH), 12.71(s, 1 H, NH), 8.67 (d, J_{H,H} = 3.25 Hz, 1 H, py ring), 8.32 (d, J_{H,H} = 4.75 Hz, 2 H, ph ring), 7.88 (d, J_{H,H} = 5.00 Hz, 1 H, py ring), 7.83 (t, 1 H, py ring), 7.50 (m, 3 H, ph ring), 7.28 (t, 1 H, py ring), 1.56 (s, 15 H, Cp* ring). **ESI-MS:** 532.10 [M⁺] peak, 494.13 [M⁺ – Cl] peak, 331.02 [Cp*Rh(2-py)⁺] peak. **UV/Vis:** λ_{max} nm (ε /10⁻⁴ M⁻¹ cm⁻¹): 255(0.45), 295(0.33), 411(0.04); **Elemental Anal.** for C₂₃H₂₆N₃OSRhClPF₆ (675.8): C 40.87 (calcd. 41.02); H 3.88 (3.97); N 6.22 (6.41).

 $[Cp*Ir(L1)Cl]PF_{6}$ (4): Yield 98 mg (64%). IR (KBr (cm⁻¹)): v(NH) 3318 m, v(CH) 2918 m, v(C=O) 1707 s, v(C=C, C=N) 1616-1477 vs, v(C=S, C-N) 1310-1229 s, v_{bent}(CH) 781-712 m, v(P-F) 843, 558 s. ¹**H** NMR (400 MHz, CDCl₃, 25 °C): δ = 13.99 (s, 1 H, NH), 12.68 (s, 1 H, NH), 8.58 (d, $J_{H,H}$ = 3.25 Hz, 1 H, py ring), 8.31 (d, $J_{H,H}$ = 4.50 Hz, 2 H, ph ring), 7.90 (t, 1 H, py ring), 7.78 (m, 2 H, ph ring), 7.56 (d, $J_{\rm H\,H}$ = 4.25 Hz, 2 H, py ring), 7.49 (t, 1 H, py ring), 1.55 (s, 15 H, Cp* ring). ESI-MS: 621.21 [M⁺] peak, 584.23 [M⁺ - Cl] peak, 420.11 [Cp*Ir(2-py)⁺] peak. UV/Vis: λ_{max} nm (ϵ / 10⁻⁴ m⁻¹ cm⁻¹): 284(0.56), 396(0.08); Elemental 255(0.57). Anal. for C23H26N3OSIrClPF6 (765.1): C 36.10 (calcd. 36.28); H 3.42 (3.57); N 5.49 (5.63).

Syntheses of Metal Complexes 5–8

A mixture of the metal precursor $[(\eta^{6}\text{-arene})\text{Ru}(\mu\text{-Cl})\text{Cl}]_{2}$ or $[\text{Cp}^{*}M(\mu\text{-Cl})\text{Cl}]_{2}$ (0.1 mmol), bis(2-pyridyl)benzoylamine (0.2 mmol) and 2.5 equivalents of NH₄PF₆ was dissolved in methanol (20 mL) and stirred at room temperature for 8 h. Yellow colored precipitate was formed. The precipitate was washed with methanol and diethyl ether (3 × 10 mL) and dried in vacuo.

[(η⁶-benzene)Ru(L2)Cl]PF₆ (5): Yield 100 mg (78%). **IR** (KBr (cm⁻¹)): v(CH) 3091 m, v(C=O) 1693 s, v(C=C, C=N) 1601–1469 vs, v(C–N) 1329–1273 s, v_{bent}(CH) 779–708 m, v(P–F) 840, 558 s. ¹H NMR (400 MHz, [d₆]-Acetone, 25 °C): δ = 9.20 (d, $J_{H,H}$ = 3.25 Hz, 2 H, py ring), 8.11 (t, 2 H, py ring), 7.88 (d, $J_{H,H}$ = 5.25 Hz, 2 H, py ring), 7.65 (t, 2 H, py ring), 7.57 (t, 1 H, ph ring), 7.53 (d, $J_{H,H}$ = 4.50 Hz, 2 H, ph ring), 7.47 (t, 2 H, ph ring), 6.35 (s, 6 H, benzene ring). **ESI-MS:** 490.11 [M⁺] peak, 455.13 [M⁺ – Cl] peak, 350.04

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[(ben)Ru(dpy)⁺] peak. **UV/Vis:** λ_{max} nm (ϵ /10⁻⁴ M⁻¹ cm⁻¹): 275(0.20); **Elemental Anal.** for C₂₃H₁₉N₃ORuClPF₆ (634.9): C 43.51 (calcd. 43.88); H 3.02 (3.30); N 6.62 (6.91).

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[(η⁶-p-cymene)Ru(L2)Cl]PF₆ (6): Yield 110 mg (79%). IR (KBr (cm⁻¹)): v(CH) 2975 m, v(C=O) 1687 s, v(C=C, C=N) 1601–1440 vs, v(C–N) 1327–1280 s, v_{bent}(CH) 780–709 m, v(P–F) 841, 558 s. ¹H NMR (400 MHz, [d₆]-Acetone, 25 °C): δ = 9.10 (d, $J_{\rm H,H}$ = 3.25 Hz, 2 H, py ring), 8.11 (t, 2 H, py ring), 7.90 (d, $J_{\rm H,H}$ = 5.00 Hz, 2 H, py ring), 7.67 (t, 2 H, py ring), 7.67 (t, 1 H, ph ring), 7.54 (d, $J_{\rm H,H}$ = 4.50 Hz, 2 H, ph ring), 7.48 (t, 2 H, ph ring), 6.30 (d, $J_{\rm H,H}$ = 4.00 Hz, 2 H, ph ring), 6.02 (d, $J_{\rm H,H}$ = 4.00 Hz, 2 H, ph ring), 3.04 (sep, 1 H, Ar_(*p*- Cy)), 1.24 (d, $J_{\rm H,H}$ = 4.25 Hz, 6 H, CH₃Ar_(*p*- Cy)), 1.24 (d, $J_{\rm H,H}$ = 4.25 Hz, 6 H, CH₃Ar_(*p*- Cy)), 1.24 (d, $J_{\rm H,H}$ = 4.25 Hz, 6 H, CH₃Ar_(*p*- Cy)), 1.24 (d, $J_{\rm H,H}$ = 4.25 Hz, 6 H, CH₃ Ar_(*p*- Cy)), 1.24 (d, $J_{\rm H,H}$ = 4.25 Hz, 6 H, CH₃ Ar_(*p*- Cy)), 1.24 (d, $J_{\rm H,H}$ = 4.25 Hz, 6 H, CH₃ Ar_(*p*- Cy)), 1.24 (d, $J_{\rm H,H}$ = 4.25 Hz, 6 H, CH₃ Ar_(*p*- Cy)), 1.24 (d, $J_{\rm H,H}$ = 4.25 Hz, 6 H, CH₃ Ar_(*p*- Cy)). ESI-MS: 546.16 [M⁺] peak, 510.09 [M⁺ – Cl] peak, 406.10 [(*p*-cy)Ru(dpy)⁺] peak. UV/Vis: $\lambda_{\rm max}$ nm (ε /10⁻⁴ m⁻¹ cm⁻¹): 269(0.22); Elemental Anal. for C₂₇H₂₇N₃ORuClPF₆ (691.0): C 46.93 (calcd. 47.28); H 3.94 (4.21); N 6.08 (6.33).

[**Cp*Rh(L2)Cl]PF₆ (7):** Yield 112 mg (80%). **IR** (KBr (cm⁻¹)): v(CH) 3120 m, v(C=O) 1676 s, v(C=C, C=N) 1600–1469 vs, v(C– N) 1326–1277 s, v_{bent}(CH) 783–715 m, v(P–F) 839, 558 s. ¹H NMR (400 MHz, [d₆]-Acetone, 25 °C): δ = 8.88 (d, J_{H,H} = 3.25 Hz, 2 H, py ring), 8.06 (t, 2 H, py ring), 7.83 (d, J_{H,H} = 5.25 Hz, 2 H, py ring), 7.66 (t, 2 H, py ring), 7.53 (t, 1 H, ph ring), 7.39 (t, 2 H, ph ring), 7.31 (d, J_{H,H} = 4.75 Hz, 2 H, ph ring),1.75 (s, 15 H, Cp* ring). **ESI-MS:** 548.20 [M⁺] peak, 512.20 [M⁺ – Cl] peak, 408.15 [Cp*Rh(dpy)⁺] peak. **UV/Vis:** λ_{max} nm (ε /10⁻⁴ M⁻¹ cm⁻¹): 230(0.35), 273(0.18), 385(0.02); **Elemental Anal.** for C₂₇H₂₈N₃ORhClPF₆ (693.8): C 46.74 (calcd. 46.98); H 4.07 (4.32); N 6.06 (6.31).

[Cp*Ir(L2)Cl]PF₆ (8): Yield 140 mg (87%). **IR** (KBr (cm⁻¹)): v(CH) 3122 m, v(C=O) 1680 s, v(C=C, C=N) 1603–1469 vs, v(C–N) 1329–1275 s, v_{bent}(CH) 782–714 m, v(P–F) 838, 558 s. ¹H NMR (400 MHz, [d₆]-Acetone, 25 °C): δ = 8.98 (d, *J*_{H,H} = 3.50 Hz, 2 H, py ring), 8.17 (t, 2 H, py ring), 8.01 (d, *J*_{H,H} = 5.00 Hz, 2 H, py ring), 7.74 (t, 2 H, py ring), 7.61 (t, 1 H, ph ring), 7.48 (t, 2 H, ph ring), 7.36 (d, *J*_{H,H} = 4.75 Hz, 2 H, ph ring), 1.76 (s, 15 H, Cp* ring). **ESI-MS:** 638.24 [M⁺] peak, 602.24 [M⁺ – Cl] peak, 498.21 [Cp*Ir(dpy)⁺] peak. **UV/Vis:** λ_{max} nm (ε /10⁻⁴ m⁻¹ cm⁻¹): 273(0.27), 376(0.02); **Elemental Anal.** for C₂₇H₂₈N₃OIrClPF₆ (783.1): C 41.41 (calcd. 41.58); H 3.60 (3.72); N 5.37 (5.51).

CCDC-1021972 (2), -1021973 (3), -1021974 (4), -1021975 (5), -102657 (6), -1026576 (7), and -1021976 (8) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by E-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033.

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Synthesis, Spectroscopic and Molecular Studies of Half-Sandwich η^6 -Arene Ruthenium, Cp* Rhodium and Cp* Iridium Metal Complexes with Bidentate Ligands