



Half-sandwich ruthenium, rhodium and iridium complexes containing dipyridyl amine based ligands

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ABSTRACT

Compounds derived from the reactions of dimeric arene ruthenium $[(\eta^6\text{-arene})\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$ (arene = benzene and *p*-cymene) and structurally analogous rhodium and iridium complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\mu\text{-Cl})\text{Cl}]_2$ (M = Rh or Ir) with 2-chloro-4,6-(di-2-pyridylamino)-1,3,5-triazine (cddt) and 2,4,6-tris(di-2-pyridylamino)-1,3,5-triazine (tdat) are reported. Compounds under investigation have been characterized by elemental analyses, NMR (^1H and ^{13}C), electronic absorption, emission spectral and electrochemical studies. Structures of the dinuclear compounds $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}]_2(\text{cddt})(\text{PF}_6)_2$, $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}]_2(\text{cddt})\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ and trinuclear compound $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}]_3(\text{tdat})\text{Cl}_3 \cdot 4\text{H}_2\text{O}$ have been determined crystallographically. Among cddt containing compounds the $(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}$ - units in $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}]_2(\text{cddt})(\text{PF}_6)_2$ are *anti*, while $(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}$ - in the rhodium compound $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}]_2(\text{cddt})\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ are *syn* with respect to triazine ring. Cyclic voltammetric studies on the compounds suggested lack of communication between the metal centres. Furthermore, although tdat is luminescent at room temperature compounds under investigation containing this ligand are non-luminescent in acetonitrile.

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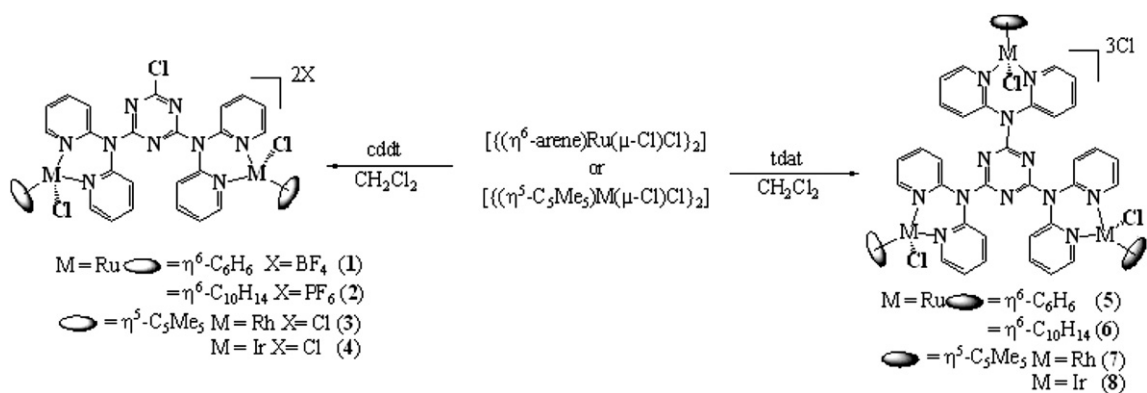
1. Introduction

The designing and synthesis of supramolecular polynuclear metal complexes have drawn immense current interest because of their possible applications as molecule-based magnets, optical devices, porous materials for gas storage, molecular recognition and catalysis etc [1–8]. Preparation of the polymetallic complexes can be achieved by reactions of metal ions/complexes using judiciously designed polydentate ligands [9–11]. Structural control of the polymeric framework is a prerequisite for obtaining specific physicochemical properties and can be tackled by the development of polydentate ligands that preorganize the metal ions in a certain spatial arrangement. In this regard, polydentate ligands containing dipyridylamine as a fragment of the extended ligand system have been developed and studied [12–16]. Further, the preparation of coordination compounds containing 1,3,5-triazine ring have received particular interest. 1,3,5-triazine moiety is a prime building unit to generate intricate coordination networks with remarkable supramolecular characteristics [17,18]. Star-shaped di-2-pyridylamino derivatives based on 1,3,5-triazine and 1,3,5-trisubstituted benzene are effective chelating ligands for a variety

of metal ions and have the potential to function as blue emitters in Organic Light Emitting Devices (OLEDs) [19–22]. In star-shaped molecules the dipyridylamino functional groups can provide binding sites for metal ions, hence allowing the development of new luminescent star-shaped coordination compounds. Novel blue luminescent star-shaped tri-dipyridylamine derivatives viz., 1,3,5-tris(di-2-pyridylamino)-benzene, 1,3,5-tris[*p*-(di-2-pyridylamino)phenyl]benzene, 2,4,6-tris(di-2-pyridylamino)-1,3,5-triazine (tdat), 2,4,6-tris[*p*-(di-2-pyridylamino)-phenyl]-1,3,5-triazine and related systems have been employed in the synthesis of a number of interesting luminescent polymetallic compounds [19–23]. Although, numerous reports dealing with the compounds based on these polydentate ligands are available in the literature, organometallic compounds imparting these ligands have scarcely been studied [20].

Furthermore, dimeric chloro-bridged arene ruthenium $[(\eta^6\text{-arene})\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$ (arene = benzene, *p*-cymene) and structurally analogous rhodium and iridium complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\mu\text{-Cl})\text{Cl}]_2$ (M = Rh or Ir) containing η^6 -/ η^5 -cyclic hydrocarbon ligands are versatile and valuable synthetic intermediates that have seen many applications in the coordination/organometallic chemistry and catalysis, polymeric materials, chiral supramolecular hosts, nano-cages and nano-particle precursors [24–34]. These undergo a rich variety of chemistry *via* the intermediacy of chloro-bridge cleavage reactions leading to the formation of a series of interesting

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Scheme 1. Synthesis of compounds 1–8.

neutral and cationic half-sandwich complexes [35–39]. With an objective to explore and develop luminescent compounds containing $\{(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}\}$ -/ $\{(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}\}$ - moieties and cddt or tdat, we have examined reactivity of $\{[(\eta^6\text{-arene})\text{Ru}(\mu\text{-Cl})\text{Cl}]_2\}$ (arene = benzene, *p*-cymene) and $\{[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\mu\text{-Cl})\text{Cl}]_2\}$ ($M = \text{Rh}, \text{Ir}$) with triazine based ligands cddt and tdat. In this paper we describe synthesis, spectral and electrochemical characterization of di/trinuclear compounds containing both the $\{(\eta^6\text{-arene})\text{RuCl}\}$ -/ $\{(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}\}$ - moieties and cddt or tdat. Also, we describe herein crystal structures of the compounds $\{[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}]_2(\text{cddt})\}(\text{PF}_6)_2$, $\{[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}]_2(\text{cddt})\}\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ and $\{[(\eta^6\text{-C}_6\text{H}_6)\text{-RuCl}]_3(\text{tdat})\}\text{Cl}_3 \cdot 4\text{H}_2\text{O}$.

2. Result and discussion

2-chloro-4,6-(di-2-pyridylamino)-1,3,5-triazine (cddt) was reported by Reedijk et al. in 2002, and any complex based on this ligand was reported by Murray et al. in 2007 [40,41]. Reactions of cddt and tdat with the dimeric arene ruthenium $\{[(\eta^6\text{-arene})\text{RuCl}(\mu\text{-Cl})]_2\}$ and structurally analogous rhodium and iridium complexes $\{[(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}(\mu\text{-Cl})]_2\}$ in dichloromethane under stirring conditions afforded di/trinuclear compounds $\{[(\eta^6\text{-C}_6\text{H}_6)$

$\text{RuCl}]_2(\text{cddt})\}(\text{BF}_4)_2$ (1), $\{[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}]_2(\text{cddt})\}(\text{PF}_6)_2$ (2), $\{[(\eta^5\text{-C}_5\text{Me}_5)\text{-RhCl}]_2(\text{cddt})\}\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (3), $\{[(\eta^6\text{-C}_6\text{H}_6)\text{-RuCl}]_3(\text{tdat})\}\text{Cl}_3 \cdot 4\text{H}_2\text{O}$ (5), $\{[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}]_3(\text{tdat})\}\text{Cl}_3$ (6), $\{[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}]_3(\text{tdat})\}\text{Cl}_3$ (7) and $\{[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}]_3(\text{tdat})\}\text{Cl}_3$ (8) in reasonably good yield. A simple scheme showing the synthesis of di/trinuclear compounds is depicted below in Scheme 1.

The compounds 1–8 are air-stable crystalline solids. Among these 1–3 are insoluble in common organic solvents like dichloromethane, chloroform, methanol, ethanol and acetone and soluble in acetonitrile, dimethylsulphoxide (DMSO) and dimethylformamide (DMF). On the other hand, 4–8 are soluble in dichloromethane, chloroform, and acetone and sparingly soluble in methanol. Characterization of 1–8 has been achieved by means of standard spectroscopic techniques (IR, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR, electronic absorption, emission spectral, and electrochemical studies) as well as satisfactory elemental analyses.

IR spectra of the respective compounds exhibited characteristic bands due to hydrocarbon ligands $\eta^6\text{-C}_6\text{H}_6$, $\eta^6\text{-C}_{10}\text{H}_{14}$, $\eta^5\text{-C}_5\text{Me}_5$ and counter anions. The $\nu(\text{C}=\text{N})$ band in these compounds shifted towards lower wave numbers and appeared at $\sim 1550\text{ cm}^{-1}$ in comparison to the free ligand ($\sim 1590\text{ cm}^{-1}$) [40]. Bands associated

Table 1
Selected crystallographic parameters.

	2	3	5
Empirical formula	$\text{C}_{43}\text{H}_{44}\text{Cl}_2\text{F}_{12}\text{N}_9\text{P}_2\text{Ru}_2$	$\text{C}_{43}\text{H}_{46}\text{Cl}_5\text{N}_9\text{O}_6\text{Rh}_2$	$\text{C}_{51}\text{H}_{42}\text{Cl}_6\text{N}_{12}\text{O}_4\text{Ru}_3$
Formula weight	1249.86	1167.96	1461.38
Temperature	293(2) K	150(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	<i>Fdd2</i>	<i>Pbca</i>	<i>P2₁/n</i>
Unit cell dimensions	<i>a</i> = 28.434(2) Å <i>b</i> = 23.8164(15) Å <i>c</i> = 16.9131(15) Å	<i>a</i> = 13.3776(13) Å <i>b</i> = 17.5831(11) Å <i>c</i> = 41.3887(19) Å	<i>a</i> = 15.4063(3) Å <i>b</i> = 15.2083(3) Å <i>c</i> = 24.2878(4) Å β = 100.968(2) $^\circ$ 5586.77(18) Å ³
Volume	11 453.4(15) Å ³	9735.4(12) Å ³	
Z	8	8	4
Density (mg/m ³)	2.174	1.594	1.737
Absorption coefficient (mm ⁻¹)	1.129	1.008	1.194
<i>F</i> (000)	7499	4720	2920
Crystal size (mm ³)	0.25 × 0.23 × 0.21	0.23 × 0.18 × 0.15	0.28 × 0.25 × 0.22
Theta range for data collection	2.95–32.49 $^\circ$	2.94–25.00 $^\circ$	3.32–25.00 $^\circ$
Index ranges	−41 ≤ <i>h</i> ≤ 37 −35 ≤ <i>k</i> ≤ 36 −25 ≤ <i>l</i> ≤ 25	−15 ≤ <i>h</i> ≤ 11 −20 ≤ <i>k</i> ≤ 20 −49 ≤ <i>l</i> ≤ 49	−18 ≤ <i>h</i> ≤ 18 −18 ≤ <i>k</i> ≤ 18 −28 ≤ <i>l</i> ≤ 28
Reflections collected	36 855	59 723	41 029
Independent reflections	9385 [R(int) = 0.0740]	8553 [R(int) = 0.1394]	9807 [R(int) = 0.0357]
Completeness to theta	94.4% (32.49 $^\circ$)	99.8% (25.00 $^\circ$)	99.7% (25.00 $^\circ$)
Data/restraints/parameters	9385/1/321	8553/0/596	9807/0/686
Goodness-of-fit on <i>F</i> ²	0.665	0.914	1.071
Final R indices [I > 2σ(I)]	R1 = 0.0758, wR2 = 0.1979	R1 = 0.0550, wR2 = 0.1349	R1 = 0.0592, wR2 = 0.1913
R indices (all data)	R1 = 0.1849, wR2 = 0.2481	R1 = 0.0822, wR2 = 0.1421	R1 = 0.0763, wR2 = 0.2010
Max. and min. transmission	0.8453, 0.8951	0.8635 and 0.8013	0.7791 and 0.7309

Table 2
Selected geometrical parameters of **2**, **3** and **5**.

2					
Ru(1)–N(4)	2.125(7)	N(4)–Ru(1)–Cg(1)	132.66		
Ru(1)–N(5)	2.130(8)	N(6)–Ru(1)–Cg(1)	121.31		
Ru(1)–Cl(2)	2.403(3)	Cl(1)–Ru(1)–Cg(1)	127.29		
Ru(1)–Cg(1)	1.697	N(4)–Ru(1)–Cl(2)	85.14(19)		
Ru(1)–C _{av}	2.183(2.157(11)– 2.227(12))	N(5)–Ru(1)–Cl(2)	86.2(3)		
		N(4)–Ru(1)–N(5)	82.9(3)		
3					
Rh(1)–N(4)	2.118(5)	Rh(2)–N(7)	2.110(5)		
Rh(1)–N(6)	2.142(5)	Rh(2)–N(9)	2.118(5)		
Rh(1)–Cl(1)	2.4038(16)	Rh(2)–Cl(2)	2.4099(16)		
Rh(1)–Cg(1)	1.7738	Rh(2)–Cg(2)	1.7727		
Rh(1)–C _{av}	2.148(2.115(6) – 2.173(6))	Rh(2)–C _{av}	2.151(2.122(6) – 2.178(6))		
N(4)–Rh(1)–Cg(1)	128.60	N(7)–Rh(2)–Cg(2)	128.09		
N(6)–Rh(1)–Cg(1)	129.69	N(9)–Rh(2)–Cg(2)	130.23		
Cl(1)–Rh(1)–Cg(1)	123.96	Cl(2)–Rh(2)–Cg(2)	124.69		
N(4)–Rh(1)–Cl(1)	89.32(14)	N(7)–Rh(2)–Cl(2)	88.34(13)		
N(6)–Rh(1)–Cl(1)	87.78(14)	N(9)–Rh(2)–Cl(2)	86.57(13)		
N(4)–Rh(1)–N(6)	83.77(18)	N(7)–Rh(2)–N(9)	84.79(18)		
5					
Cg(8)–Ru(1)	1.6538	Cg(9)–Ru(2)	1.6690	Cg(10)–Ru(3)	1.6721
N(4)–Ru(1)	2.094(7)	Cl(2)–Ru(2)	2.3907(19)	N(12)–Ru(3)	2.104(6)
Cl(1)–Ru(1)	2.385(2)	N(7)–Ru(2)	2.106(6)	Cl(3)–Ru(3)	2.4094(18)
N(6)–Ru(1)	2.089(7)	N(9)–Ru(2)	2.109(6)	N(10)–Ru(3)	2.089(6)
Ru(1)–C _{av}	2.164(2.145(9)– 2.190(12))	Ru(2)–C _{av}	2.176(2.163(8)– 2.194(8))	Ru(3)–C _{av}	2.184(2.155(8)– 2.207(8))
Cg(8)–Ru(1)–Cl(1)	128.67	Cg(9)–Ru(2)–N(9)	127.62	Cg(10)–Ru(3)–Cl(3)	127.96
Cg(8)–Ru(1)–N(4)	133.57	Cg(9)–Ru(2)–Cl(2)	127.50	Cg(10)–Ru(3)–N(10)	128.29
Cg(8)–Ru(1)–N(6)	123.93	Cg(9)–Ru(2)–N(7)	130.51	Cg(10)–Ru(3)–N(12)	128.37
Cl(1)–Ru(1)–N(4)	84.29(17)	N(7)–Ru(2)–N(9)	83.6(2)	Cl(3)–Ru(3)–N(10)	87.64(17)
Cl(1)–Ru(1)–N(6)	85.96(18)	Cl(2)–Ru(2)–N(7)	85.41(16)	Cl(3)–Ru(3)–N(12)	87.22(17)
N(4)–Ru(1)–N(6)	84.5(3)	Cl(2)–Ru(2)–N(9)	86.81(17)	N(10)–Ru(3)–N(12)	82.3(2)

with pyridyl ring vibrations appeared at $\sim 1030\text{ cm}^{-1}$. Shift in the position of $\nu(\text{C}=\text{N})$ corresponding to pyridyl ring vibrations suggested the coordination of ligand to metal ion through pyridyl ring nitrogen. In addition, bands corresponding to the counter anion BF_4^- and PF_6^- appeared at ~ 1120 and 840 cm^{-1} in the spectra of respective compounds.

2.1. Molecular structures

Structures of the dinuclear compounds **2**, **3** and trinuclear compound **5** have been determined crystallographically. Selected crystallographic data and geometrical parameters are summarized in Tables 1 and 2, respectively. Crystal structure of the complexes with atom numbering scheme is shown in Figs. 1–3. It is worth

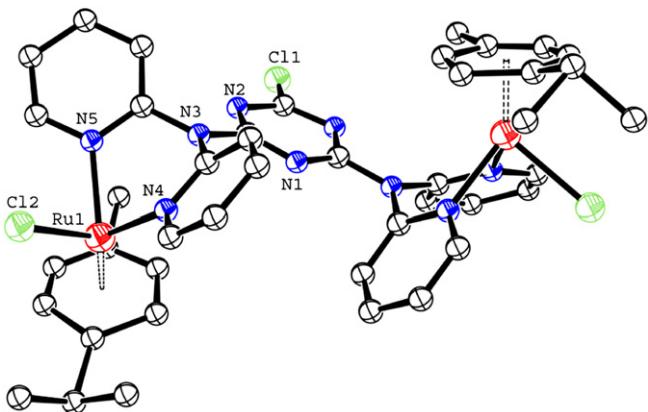


Fig. 1. Cation of **2** at 30% thermal ellipsoid probability (symmetric atoms are generated by symmetry operation $= -x + 1/2, -y + 1/2, z$).

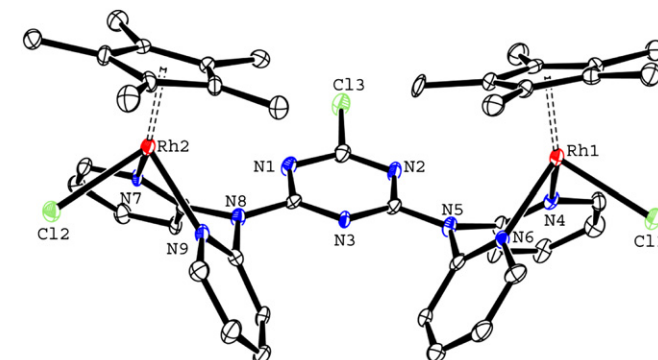


Fig. 2. Cation of **3** at 30% thermal ellipsoid probability (H atoms excluded for clarity).

mentioning that although crystal data of **2** is not good enough, however it strongly supported the formation of the complex **2**.

Compounds **2** and **3** crystallize in orthorhombic crystal system and *Fdd2* and *Pbca* space groups. In these compounds the metal centre exhibited a typical *piano-stool* geometry coordinated by the hydrocarbon ligands $\text{C}_{10}\text{H}_{14}$ in η^6 - or C_5Me_5 in η^5 -manner, a chloride and two nitrogen atoms from the *cdtt* or *tdat* in κ^2 -manner. Complex **2** has two fold symmetry axis and symmetrical atoms have been generated by symmetry operation $-x + 1/2, -y + 1/2, z$. The average Ru–C distances in **2** are 2.183 Å [range 2.157(11)–2.227(12) Å] and centroid of the *p*-cymene ring is separated from the Ru centre by 1.697 Å. The N–Ru–N and N–Ru–Cl angles are less than 90° [85.14(19), 86.2(3) and 82.9(3) $^\circ$] and consistent with the “*piano stool*” arrangement of various groups about the metal centre. The Ru–N and Ru–Cl bond distances are normal and are 2.125(7), 2.130(8) and 2.403(3) Å, respectively [42]. Similarly in complex **3**

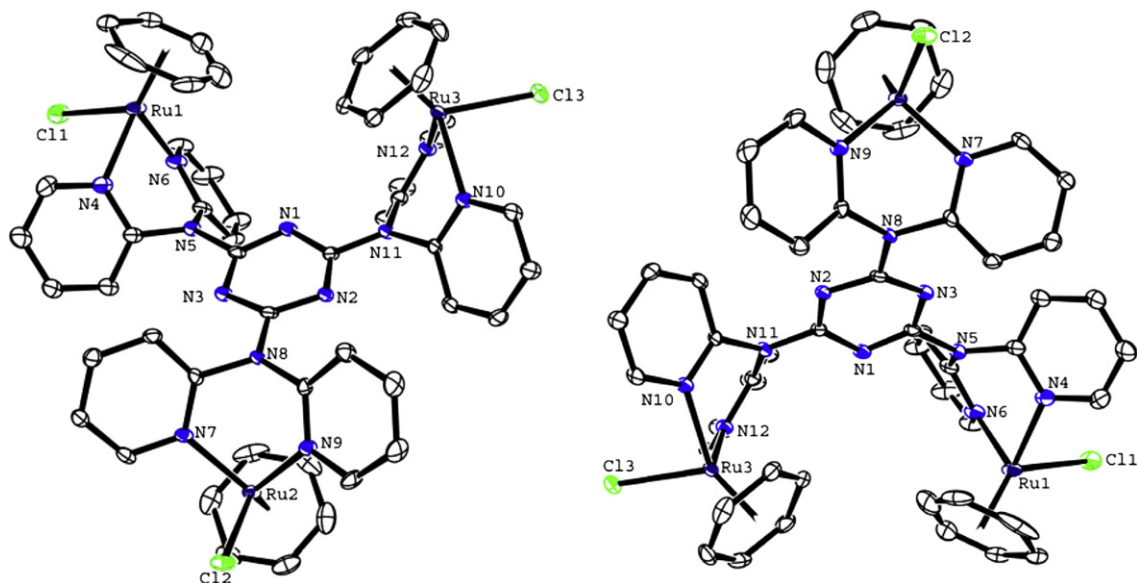


Fig. 3. Cation of **5** at 30% thermal ellipsoid probability (H atoms excluded for clarity).

average Rh–C distances are 2.148 Å [range 2.115(6)–2.173(6) Å] for Rh1 and 2.151 Å [range 2.122(6)–2.178(6) Å] for Rh2 [Table 3] (Fig. 2). The Rh–Cl and Rh–N bond distances are comparable to those in other related complexes [43,44]. In addition to two chloride counter ions, there are six water of crystallization in each unit of the compound **3** which results in water channels discussed later [45]. Interestingly, in the complex cation of **2**, two $\{(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}\}$ -units are ‘anti’- while two $\{(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}\}$ -units in **3** are ‘syn’-with respect to the triazine ring (Fig. S1) [28].

Compound **5** crystallizes in monoclinic system with $P2_1/n$ space group and contains three chlorides as the counter ions and 4 water molecules. Free ligand has propeller shaped geometry [23]. After coordination to the arene precursor to minimize the steric hindrance it adopted a geometry in which two $\{(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}\}$ - moieties are ‘syn’ and one is ‘anti’(Fig. S1) with respect to the triazine ring plane which is similar to “up and down structure” observed in the palladium complex $[(\text{Pd}(\text{OAc})_2)_3(\text{tdat})]$ [55]. The geometry about each metal centre is similar to that in **2**, except that there are three $\{(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}\}$ - units instead of two units of $\{(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}\}$ -. The Ru–N, Ru–C and Ru–Cl bond distances and various angles support “piano stool” geometry about the metal centre and are close to the one reported in other closely related complexes [43,44]. In these complexes the amine nitrogen of dipyrindylamine has trigonal planar geometry as in the free ligand tdat (Fig. S1) [45–55]. It may be

attributed to the involvement of lone pair of electrons on secondary amine in conjugation with the central triazine ring.

2.2. NMR spectral studies

^1H NMR spectra of the compounds displayed resonances associated with the pyridyl ring protons of respective ligands and resonances corresponding to $\eta^6\text{-C}_6\text{H}_6$, $\eta^6\text{-C}_{10}\text{H}_{14}$ or $\eta^5\text{-C}_5\text{Me}_5$ ring protons. Resulting data along with other characterization data is summarized in Section 4. The position and integrated intensity of the various signals associated with the ligands and precursors corroborated well to a system involving coordination of ligand to the metal centres. ^1H NMR of the ligands cddt and tdat exhibits four peaks (Fig. S2) [40]. In the spectra of ruthenium compounds **1**, **2** (cddt) **5** and **6** (tdat) signals associated with the pyridyl protons of ligand displayed a downfield shift and resonated as a broad singlet instead of multiplets in comparison to the uncoordinated ligands. On the other hand, in the compounds based on rhodium **3**, **7** and iridium **4** and **8** also, the pyridyl protons exhibited a downfield shift and an increase in the number of signals in comparison to the uncoordinated ligands. Expected number of resonances in the cddt complexes is 8, while 12 signals are expected in tdat compounds. The presence of only four peaks in the ^1H NMR spectra of ruthenium compounds suggested that probably their structures are not completely retained in DMSO solution at room temperature while, rhodium and iridium are quite stable (Fig. S2). ^1H NMR spectra of **1** and **4** exhibited a broad and strong signal associated with the coordinated benzene ($\delta = 6.0$ ppm) while, 2–3 signals appeared in the spectra of **3**, **4**, **7** and **8** ($\delta \sim 1\text{--}2$ ppm) for pentamethylcyclopentadienyl protons, which also supported the retention of structure of Rh/Ir complexes in solution. The ^1H NMR spectrum of **2** and **6** exhibited a doublet at $\delta = 1.13$ and a septet at $\delta = 2.81$ for the protons of isopropyl group and two doublets at $\delta = 6.37\text{--}6.20$ ppm corresponding to aromatic *p*-cymene ring CH protons.

^{13}C NMR spectra of the compounds have been recorded in DMSO at room temperature. Representative, ^{13}C NMR spectra of **2** is depicted in Fig. S3. Although the ^{13}C NMR spectral could not provide any valuable information about the linkage of ligands to respective metal centre, the presence of signals associated with both the carbons of ligand and precursors supported its

Table 3
Electrochemical data for homo binuclear complexes in acetonitrile solution at (rt), scan rate 100 mV/s.

Complexes	Oxidation E°_{298} (V)		Reduction E°_{298} (V)		
	I	II	I	II	III
cddt			–0.82	–1.12(106)	–1.34
tdat			–0.86	–1.14(117)	–1.36
1	0.41	1.52	–0.92	–1.14(110)	–1.36
2	0.62		–0.91	–1.13(117)	–1.35
3	0.86		–0.87	–1.13(177)	–1.36
4	0.79		–0.94	–1.02(140)	–1.38
5	0.51			–1.06	–1.28
6	0.69	1.46		–1.12(100)	–1.35
7	0.82			–1.10(66)	–1.37
8	0.77			–1.10(143)	–1.36

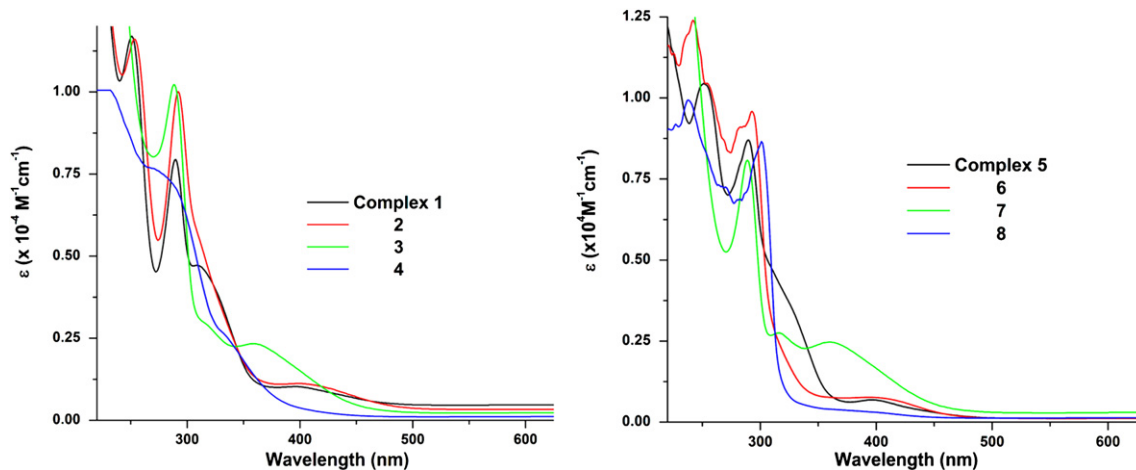


Fig. 4. UV-vis absorption spectra of 1–8.

complexation to the metal centre and peak intensities provided a clear view about the ratio in which the precursors binds with the ligand. The resonances corresponding to ligand carbons (Section 4) appeared in aromatic region and were slightly downfield shifted in comparison to the uncoordinated ligands.

2.3. Electronic spectral studies

Absorption spectra of all the compounds were acquired in acetonitrile and resulting data is summarized in the experimental section. In these complexes the metal centre has d^6 configuration and provides filled metal orbitals of proper symmetry to interact with the relatively low lying π^* orbitals on the ligand cddt or tdat. It is expected to give a band associated with metal to ligand charge transfer (MLCT) transition ($t_1g \rightarrow \pi^*$) whose position varies with the nature of metal ion. The electronic spectra of ruthenium complexes displayed bands in the low energy side at ~ 400 nm and rhodium complexes at ~ 369 nm, respectively (Fig. 4). On the basis of its position and intensity these bands has been assigned to MLCT ($M_d\pi \rightarrow \pi^*$) transitions while, the absorptions between 330 and 240 nm to the ligand field or intra-ligand transitions ($\pi \rightarrow \pi^*$) [42]. Comparison of the electronic spectra of dinuclear compounds with those of the trinuclear compounds revealed that there is no major change in the peak position, extinction coefficient and number of peaks. This observation is consistent with fact that there is no interaction between metal centres suggesting that these are present in similar electronic environment.

2.4. Emission spectral studies

Emission experiments were performed in acetonitrile at RT. The uncoordinated 2,4,6-tris(di-2-pyridylamino)-1,3,5-triazine (tdat) displays an intense blue fluorescent emission in acetonitrile solution at room temperature with the emission maxima at 415 nm. Some of its complexes are bright photoluminescent blue emitters with well defined glass transition points [19,23]. In sharp contrast, compounds 5–8 upon excitation at their respective lowest energy bands did not exhibit any emission (detection limit = 0.1%). The absence of fluorescence may be attributed to some *non-radiative pathways* which may lead to deactivation of the excited state. At this stage we are not in a position to make specific comments in this regard.

2.5. Electrochemistry

Cyclic voltammetric studies on 1–8 were performed in acetonitrile at room temperature (scan rate 100 mV/s), resulting data is summarized in Table 3 and voltammograms for 1–8 are depicted in the Fig. S4 (Supporting Information). In the anodic potential window (0 to +2 vs. Ag/Ag^+) the ruthenium compounds 1, 2, 4 and 6 exhibited irreversible peaks at +0.41, +0.62, +0.51, and +0.69 V respectively, while rhodium compounds 3, 7 and iridium compounds 4, 8 displayed peaks at +0.86, +0.82 and +0.79, +0.77 V, respectively. These may be attributed to metal based Ru (II/III), Rh(III/IV) and Ir(III/IV) oxidations. Further, 1 and 6 displayed additional peaks at +1.52 and +1.46 V, respectively which may be due to the second oxidation of ruthenium involving Ru(III/IV) process [42]. The presence of only one oxidation peak may be due to oxidation of the metal centres at almost the same potential as arrangement of various groups about the metal centres are the same and overall electronic environments are very close therefore, these oxidize at the same potential. It is observed that with the increase in number of metal centre, there is neither shift in the position nor increase in number in redox processes. It suggested lack of communication between the metal centres through the ligand. On the other hand, in cathodic potential window (0 to –2 vs. Ag/Ag^+) both the cddt and tdat containing compounds exhibited three ligand based reductions at ~ -0.92 , -1.12 , -1.36 V (Fig. S4).

2.6. Weak interaction studies

Matrices for weak bonding interactions in 2, 3 and 5 are gathered in Table S1 (see supporting information). Crystal structure of 2

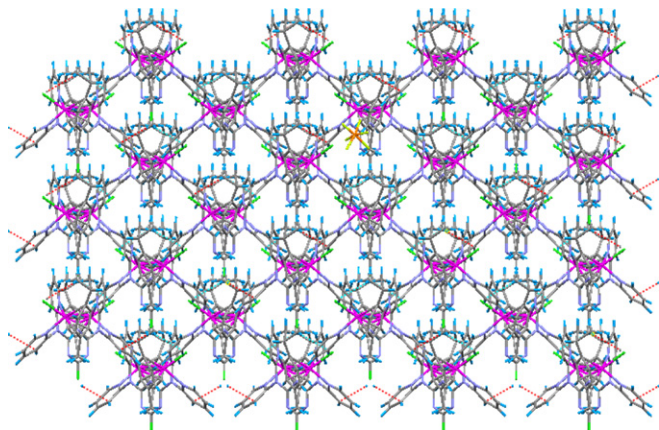


Fig. 5. Packing view of 2 along 'a' axis.

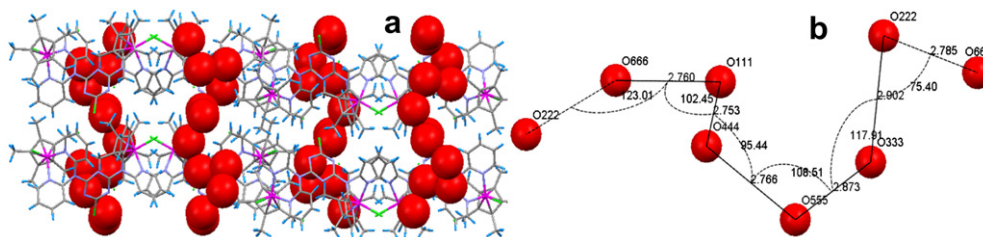


Fig. 6. Water channel in **2c** (a) view along 'a' axis (b) distances and angles in water channel (solid red spheres shows water molecules).

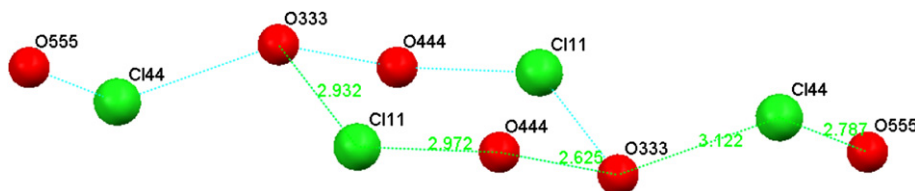


Fig. 7. Solvent and counter ion assembled cluster in complex **5**.

revealed the presence of extensive intermolecular C–H···Cl and C–H···F interactions. It is well established that these types of interactions play an important role in the construction of huge supramolecular architectures. Fig. 5 shows packing view of **2** along crystallographic 'a' axis.

Furthermore, in compound **3** six water molecules are present per unit of the complex. Crystal structure revealed the presence of zig-zag hydrogen-bonded network in the lattice (Fig. 6a). The O–O distances range from 2.753 to 2.902 Å, (O111–O666 = 2.760 Å, O444–O555 = 2.766 Å, O333–O222 = 2.902 Å, O111–O444 = 2.753 Å, O333–O555 = 2.873 Å, O222–O666 = 2.785 Å) indicating moderate to strong hydrogen bonding interactions and the hydrogen-bonded O–O–O angles range from 75.40° (O333–O222–O666) to 123.01° (O222–O666–O111), both the distances and angles are in the range found in ice and water clusters (Fig. 6b) [56–64]. In addition, the oxygen atom O3w is H bonded to the chloride Cl(4), further stabilizing the unusual architecture (3.126–3.210 Å) (O222–Cl4 = 3.210 Å, O111–Cl4 = 3.168 Å, O666–Cl1 = 3.187 Å, O444–Cl5 = 3.126 Å, O222–Cl5 = 3.156 Å).

Similarly, in complex **5**, there are four water molecules and three chlorides which, also leads to the supramolecular channel. Fig. 7 shows that the interaction between water and chloride ions leading to cyclohexane type chair structure. The O444–O333 distance is 2.625 Å, indicating strong hydrogen bonding (Fig. S11) In addition, the oxygen atom and chloride ion Cl(4), further stabilizes the unusual architecture (2.787–3.122 Å) (O333–Cl44 = 3.122 Å, O333–Cl11 = 2.932 Å, O444–Cl11 = 2.972 Å). The involvement of molecular water chains as "proton wires" in biological systems is of eminent importance and is receiving great attention from the scientific community.

3. Conclusion

Through this work we have presented the syntheses and characterization of first examples of the organometallic complexes containing both the $\{(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}\}$ – $\{(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}\}$ moieties and 2-chloro-4,6-(di-2-pyridylamino)-1,3,5-triazine (cddt) and 2,4,6-tris(di-2-pyridylamino)-1,3,5-triazine (tdat). From the structural studies it has been shown that among cddt containing complexes the $\{(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}\}$ – units in $\{[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}]_2(\text{cddt})(\text{PF}_6)_2\}$ are *anti*, while $\{(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}\}$ – units in the

rhodium complex $\{[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}]_2(\text{cddt})\}\text{Cl}_2\cdot 6\text{H}_2\text{O}$ **3** are *syn* with respect to triazine ring. Cyclic voltammetric studies on the complexes suggested lack of communication between the metal centres. Furthermore, although tdat is luminescent at room temperature complexes under investigation derived from this ligand are non-luminescent.

4. Experimental section

Reagents: All the synthetic manipulations were performed under nitrogen atmosphere in deaerated solvents. Cyanuric chloride, 2,2'-dipyridylamine (dpa), ammonium hexafluoro phosphate, ammonium tetrafluoroborate, tetrabutylammonium perchlorate, diisopropylethylamine, 1,3-cyclohexadiene, α -phellandrene and ruthenium(III) chloride hydrate, rhodium(III) chloride hydrate and iridium(III) chloride hydrate (all Aldrich) were used as received without further purifications. The ligands 2-chloro-4,6-(di-2-pyridylamino)-1,3,5-triazine (cddt), 2,4,6-tris(di-2-pyridylamino)-1,3,5-triazine (tdat) and precursor complexes $\{[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}(\mu\text{-Cl})_2]\}$, $\{[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}(\mu\text{-Cl})_2]\}$, $\{[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}(\mu\text{-Cl})_2]\}$ and $\{[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}(\mu\text{-Cl})_2]\}$ were prepared and purified following the literature procedures [40,65–69].

General methods: Elemental analyses for C, H and N were performed on Exeter Analytical Inc. Model CE-440 CHN analyzer. Infrared spectra in KBr pellets were acquired on a Varian 3100 FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL AL 300 MHz spectrometer at room temperature (RT) using d_6 -DMSO as the solvent and TMS as an internal reference. Electronic and emission spectral data were acquired on a Shimadzu UV-1700 series and Carry Eclipse Luminescence spectro-photometers, respectively. Cyclic voltammetric measurements were performed on a CHI 620c electrochemical analyzer. A glassy carbon working electrode, platinum wire auxiliary electrode, and Ag/Ag⁺ reference electrode were used in a standard three-electrode configuration. Tetrabutylammonium perchlorate (TBAP) was used as a supporting electrolyte, and the solution concentration was about 10^{-3} M.

4.1. Synthesis of $\{[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}]_2(\text{cddt})(\text{BF}_4)_2\}$ (**1**)

To a suspension of $\{[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}(\mu\text{-Cl})_2]\}$, (0.125 g, 0.25 mmol) in dichloromethane (15 mL) cddt (0.114 g, 0.25 mmol) was added and stirred for 5 h at room temperature. Slowly, it dissolved and

gave a yellow solution. After filtration solvent was removed under reduced pressure and residue was extracted with methanol and filtered. A saturated solution of ammonium tetrafluoroborate in methanol was added to the filtrate. After a couple of hours micro-crystalline yellow product appeared which was separated by filtration, washed with diethyl ether and dried *in vacuo*. Yield: 0.145 g, 55%. Anal. Calcd. for $C_{35}Cl_3F_8H_{28}N_9B_2Ru_2$ (M.W. = 1056.77): C, 39.78; H, 2.67; N, 11.93. Found: C, 40.31; H, 2.74; N, 5.21%. 1H NMR (δ ppm): 5.99 (s, 12H), 7.32 (m, 4H), 7.62 (br s, 4H), 7.93 (br s, 4H), 8.94 (m, 4H), ^{13}C NMR (δ ppm): 102.4 ($\eta^6-C_6H_6$), 125.6, 126.1, 140.8, 150.9, 155.3, 164.2 (cddt). UV–vis. (CH_3CN , λ_{max} nm, ϵ): 402 (1.12×10^3), 292 (1.00×10^4), 253 (1.16×10^4).

4.2. Synthesis of $[(\eta^6-C_{10}H_{14})RuCl]_2(cddt)(PF_6)_2$ (**2**)

Compound **2** was prepared using $[(\eta^6-C_{10}H_{14})RuCl(\mu-Cl)]_2$, (0.153 g, 0.25 mmol) in place of $[(\eta^6-C_6H_6)RuCl(\mu-Cl)]_2$, and ammonium hexafluorophosphate in place of ammonium tetrafluoroborate following the above procedure for **1**. Crystals suitable for single crystal X-ray diffraction analyses were obtained by slow evaporation of acetonitrile solution of **2**. Yield: 0.193 g, 60%. Anal. Calcd. For $C_{43}Cl_3F_{12}H_{44}N_9P_2Ru_2$ (M.W. = 1285.31): C, 40.18; H, 3.45; N, 9.81. Found: C, 39.98; H, 3.23; N, 9.92%. 1H NMR (δ ppm): 1.28 (d, 12H, $J = 6.3$ Hz, $CH(CH_3)_2$), 1.84 (s, 6H, CH_3), 2.82 (m, 2H, $CH(CH_3)_2$), 5.69 (m, 4H, ar *p*-cym), 6.01 (m, 4H, ar *p*-cym), 7.67 (m, 4H), 7.94 (br s, 4H), 8.12 (br s, 4H), 8.84 (m, 4H), ^{13}C NMR (δ ppm): 17.7, 22.2, 30.1, 82.0, 86.5, 101.7, 103.6 (*p*-cym), 125.2, 125.9, 141.0, 150.7, 155.0, 164.1 (cddt). UV–vis. (CH_3CN , λ_{max} nm, ϵ): 398 (1.03×10^3), 309 (4.72×10^3), 290 (7.94×10^3), 253 (1.17×10^4).

4.3. Synthesis of $[(\eta^5-C_5Me_5)RhCl]_2(cddt)(Cl)_2 \cdot 6H_2O$ (**3**)

This compound was prepared using $[(\eta^5-C_5Me_5)RhCl(\mu-Cl)]_2$, (0.154 g, 0.25 mmol) and cddt (0.114 g, 0.25 mmol) following the method for **1**. It was separated as reddish yellow solid. Crystals suitable for single crystal X-ray analyses were obtained by the slow evaporation of acetonitrile solution of **3**. Yield: 0.181 g, 62%. Anal. Calcd. for $C_{43}Cl_5H_{46}N_9Rh_2O_6$ (M.W. = 1167.98): C, 48.18; H, 4.33; N, 11.76. Found: C, 48.35; H, 4.21; N, 11.53%. 1H NMR (δ ppm): 1.46 (s, 12H of water), 1.55 (s, 30H), 7.36 (m, 4H), 7.61 (m, 4H), 8.23 (m, 4H), 8.76 (m, 4H), ^{13}C NMR (δ ppm): 8.4, 79.7 (C_5Me_5), 125.2, 125.9, 137.7, 153.9, 157.3, 168.8 (cddt). UV–vis. (CH_3CN , λ_{max} nm, ϵ): 360 (2.24×10^3), 315 (2.98×10^3), 288 (1.02×10^4).

4.4. Synthesis of $[(\eta^6-C_5Me_5)IrCl]_2(cddt)(Cl)_2$ (**4**)

It was prepared following the procedure employed for **1** using $[(\eta^6-C_5Me_5)IrCl(\mu-Cl)]_2$ (0.199 g, 0.25 mmol). Yield: 0.168 g, 63%. Anal. Calcd. for $C_{43}Cl_5H_{46}N_9Ir_2$ (M.W. = 1250.58): C, 48.18; H, 4.33; N, 11.76%. Found: C, 48.35; H, 4.21; N, 11.53%. 1H NMR (δ ppm): 1.46 (s, 12H), 1.55 (s, 30H), 7.36 (m, 4H), 7.61 (m, 4H), 8.23 (m, 4H), 8.76 (m, 4H), ^{13}C NMR (δ ppm): 8.4, 79.7 (C_5Me_5), 125.2, 125.9, 137.7, 153.9, 157.3, 168.8 (cddt). UV–vis. (CH_3CN , λ_{max} nm, ϵ): 332 (2.66×10^3), 283 (7.94×10^3), 253 (1.17×10^4).

4.5. Synthesis of $[(\eta^6-C_6H_6)RuCl]_3(tdat)(Cl)_3 \cdot 4H_2O$ (**5**)

It was prepared following the procedure employed for **1** using $[(\eta^6-C_6H_6)RuCl(\mu-Cl)]_2$, (0.375 g, 0.75 mmol) and tdat (0.294 g, 0.50 mmol). Yield: 0.411 g, 55%. Anal. Calcd. for $C_{57}H_{65}Cl_6N_{12}O_4Ru_3$ (M.W. = 1498.13): C, 45.70; H, 4.37; N, 11.22. Found: C, 45.31; H, 4.04; N, 11.11%. IR (KBr, cm^{-1}): 1606 (m); 1579 (w); 1553 (m); 1482 (m); 1467 (m); 1320 (m); 1300 (m); 1276 (m); 1252 (m); 1160 (m). 1H NMR (δ ppm): 6.12 (s, 18H C_6H_6), 7.60 (t, 6H, $J = 6.3$ Hz), 7.93 (br s, 6H), 8.60 (br s, 6H), 8.91 (s, 6H). ^{13}C NMR (δ ppm): 86.43 (C_6H_6),

125.0, 126.2, 135.3, 140.5, 151.2, 155.3 (ligand). UV–vis. (CH_3CN , λ_{max} nm, ϵ): 400 (7.57×10^2), 293 (9.59×10^3), 283 (9.11×10^3), 242 (1.24×10^4).

4.6. Synthesis of $[(\eta^6-C_{10}H_{14})RuCl]_3(tdat)(Cl)_3$ (**6**)

It was prepared following the procedure adopted for **5** except that $[(\eta^6-C_{10}H_{14})RuCl(\mu-Cl)]_2$ (0.459 g, 0.75 mmol) was used in place of $[(\eta^6-C_6H_6)RuCl(\mu-Cl)]_2$. Yield: 0.478 g, 60%. Anal. Calcd. For $C_{69}H_{81}Cl_6N_{12}Ru_3$ (M.W. = 1594.39): C, 51.98; H, 5.12; N, 10.54. Found: C, 51.60; H, 4.97; N, 10.42%. 1H NMR (DMSO, δ ppm): 1.34 (br s, 18H), 1.85 (s, 9H), 2.82 (m, 3H), 6.015 (br s, 6H), 6.28 (br s, 6H), 7.62 (t, 6H, $J = 6.3$ Hz), 7.93–8.5 (br signal, 12H), 8.79 (d, 6H, $J = 4.5$ Hz). ^{13}C NMR (DMSO, δ ppm): 18.1, 22.3, 30.0, 81.4, 88.1, 101.9, 102.6 (*p*-cymene), 125.1, 126.2, 140.3, 151.4, 154.4, 164.2 (tdat). UV–vis. (CH_3CN , λ_{max} nm, ϵ): 395 (6.85×10^2), 290 (8.7×10^3), 251 (1.04×10^3).

4.7. Synthesis of $[(\eta^5-C_5Me_5)RhCl]_3(tdat)(Cl)_3$ (**7**)

Compound **7** was prepared following the procedure employed for **5** except using $[(\eta^5-C_5Me_5)RhCl(\mu-Cl)]_2$ (0.464 g, 0.75 mmol) and tdat. Yield: 0.505 g, 63%. Anal. Calcd. for $C_{69}H_{86}Cl_6N_{12}Rh_3$ (M.W. = 1604.94): C, 51.64; H, 5.40; N, 10.47. Found: C, 51.42; H, 5.21; N, 10.53%. 1H NMR (δ ppm): 1.46 (s, 15H), 1.58 (s, 15H), 1.63 (s, 15H), 7.23 (br s, 4H), 7.48 (t, 2H, $J = 7.5$ Hz), 7.65 (d, 4H, 5.7 Hz), 7.82 (s, 2H), 7.91 (s, 2H), 8.12 (s, 4H), 8.31 (s, 4H), 8.68 (d, 4H, $J = 11.7$ Hz). ^{13}C NMR (δ ppm): 8.5, 96.6, 98.9, 118.1, 121.6, 122.6, 137.7, 148.4 (tdat). UV–vis. (CH_3CN , λ_{max} nm, ϵ): 360 (2.47×10^3), 316 (2.75×10^3), 289 (8.08×10^3).

4.8. Synthesis of $[(\eta^5-C_5Me_5)IrCl]_3(tdat)(Cl)_3$ (**8**)

A synthetic procedure similar to that for **1** was employed for preparing **8** using $[(\eta^5-C_5Me_5)IrCl(\mu-Cl)]_2$ (0.597 g, 0.75 mmol) and tdat (0.294 g, 0.50 mmol). Yield: 0.571 g, 61%. Anal. Calcd. for $C_{69}H_{86}Cl_6Ir_3N_{12}$ (M.W. = 1872.87): C, 44.25; H, 4.63; N, 8.97. Found: C, 44.02; H, 4.21; N, 8.53%. 1H NMR (δ ppm): 1.63 (s, 45H), 7.07 (d, 2H, $J = 7.8$ Hz), 7.26 (s, 4H), 7.57 (s, 4H), 7.71 (d, 2H, $J = 7.5$ Hz), 8.04 (br s, 4H), 8.63 (s, 4H), 8.97 (d, 4H, $J = 7.5$ Hz), ^{13}C NMR (δ ppm): 8.0, 88.40 (C_5Me_5), 114.2, 122.6, 125.7, 141.3, 148.6, 150.0 (tdat). UV–vis. (CH_3CN , λ_{max} nm, ϵ): 301 (8.66×10^3), 238 (9.93×10^3).

X-ray structure determinations: Crystals suitable for single crystal X-ray diffraction analyses for **2**, **3** and **5** were grown by slow evaporation of acetonitrile solution of the respective compounds. Preliminary data on the space group and unit cell dimensions as well as intensity data were collected on Oxford Diffraction XCALIBUR-S using graphite monochromatized Mo-K α radiation by use of ω scans. The structures were solved by direct methods and refined by using SHELX-97 [70,71]. Non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were geometrically fixed and allowed to refine using a riding model. PLATON was used for analyzing the interaction and stacking distances [72].

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Appendix A. Supporting information

CCDC reference numbers 723330 (**2**), 723331 (**3**) and 761883 (**5**) for crystallographic data in CIF. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found in the on-line version, at doi:10.1016/j.jorganchem.2010.04.022.

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