

REGULAR ARTICLE

Half-sandwich ruthenium, rhodium and iridium complexes of triazolopyridine ligand: Synthesis and structural studies

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Abstract. Triazolopyridine ligand, {3-(2-pyridyl)-[1,2,3]triazolo[1,5-a]-pyridine}, **L** was synthesized by reaction of *p*-toulenesulphonyl hydrazine and dipyriddy ketone in the presence of acetic acid. Half-sandwich ruthenium, rhodium and iridium complexes [**1–4**] have been synthesized by reaction of [(arene)MCl₂]₂ (arene = *p*-cymene/benzene/Cp* and M = Ru/Rh/Ir) with ligand **L** in methanol. The reaction in 1:2 (M:L) ratio has yielded all mononuclear cationic complexes such as [(arene)MLκ_N²Cl]PF₆, where {(arene)M} = (*p*-cym)Ru (**1**), (benz)Ru (**2**), Cp*Rh (**3**) and Cp*Ir (**4**). All the complexes were characterized by spectral studies and the solid state structures of complexes, **1** and **3** were unambiguously determined by crystallographic studies.

Keywords. triazolopyridine; ruthenium; rhodium; iridium.

1. Introduction

Platinum group metals containing heterocyclic nitrogen based ligands exhibit significant photochemical properties, catalytic activities, electrochemical behaviour as well as cytotoxic activities.^{1–9} Triazolopyridine structures are fundamental building blocks for numerous pharmaceutical and functional materials.¹⁰ In general, the ligand under study *i.e.*, [1,2,3]triazolo[1,5-a]pyridines have been synthesized by the oxidative cyclization of 2-pyridyl ketone hydrazones by using oxidants such as Pb(OAc)₂, copper salts, MnO₂, hypervalent iodine, Ag₂O, Ni peroxide, *etc.*^{11–15} Synthesis of this ligand is also possible by the reaction of 2-pyridyl ketone with tosylhydrazine in NaOH.¹⁶ In our attempt to prepare a Schiff base by condensing tosylhydrazine with dipyriddy ketone using glacial acetic acid, we ended up with the triazolopyridine. Curiously, this ring system has been ignored as a ligand in coordination chemistry. There have been only a few reports of complexes with a [1,2,3]triazolo[1,5-a] pyridine unit acting as a donor to a metal centre.^{17–21} Ruthenium complexes of the ligand under study were synthesized containing 2,2'-bipyridine (bipy) auxiliary ligands and their electrochemistry were delineated.²² Hitherto, we have synthesized numerous arene metal complexes of various nitrogen donor ligands and explored their structures and various bonding modes.^{23,24}

According to our knowledge, there are no reports of complexes of arene metal complexes with the ligand under study. We have synthesized and characterized the ruthenium, rhodium and iridium arene complexes with this ligand [1,2,3]triazolo[1,5-a] pyridine (**L**).

2. Experimental

2.1 Materials and methods

All the reactions were carried out without using any inert atmosphere. Metal halides MCl₃(H₂O)_n (M = Ru, Rh and Ir) were purchased from Arora Matthey Limited. Pentamethylcyclopentadiene (Sigma-Aldrich), α -Phellandrene (Merck), *p*-toluene sulphonyl hydrazine (Sigma-Aldrich), dipyriddy ketone (Sigma-Aldrich), silica gel (Hi-Media) were used as received. All the solvents used for syntheses were dried and distilled prior to use according to the standard procedures and stored over activated molecular sieves.²⁵ Dichloromethane, chloroform and hexane were dried over calcium chloride and methanol was dried using calcium oxide. Precursor compounds of ruthenium, rhodium and iridium were prepared according to the literature methods.^{26,27} Infrared (IR) spectra were recorded on a Perkin-Elmer 983 spectrophotometer with the compounds dispersed in KBr discs. ¹H NMR spectra were recorded with Bruker Avance II 400 MHz spectrometer. Chemical shifts for ¹H NMR are reported using tetramethylsilane (TMS) as the internal standard and were recorded in deuterated dimethyl sulphoxide (DMSO-d₆). UV-Vis spectra were recorded by using Perkin-Elmer lambda 25 spectrophotometer. Mass spectra were recorded on Q-T of APCI-MS HAB 273 instrument.

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$J_{\text{HH}} = 8$ Hz), 8.76 (d, 1H, $J_{\text{HH}} = 8$ Hz), 8.55 (d, 1H, $J_{\text{HH}} = 8$ Hz), 8.29 (t, 1H, $J_{\text{HH}} = 8$ Hz), 7.97 (t, 1H, $J_{\text{HH}} = 8$ Hz), 7.69 (m, 2H), 5.56 (s, 6H). UV-Vis (MeOH) λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) = 221 (9.0×10^4), 293 (7.10×10^4), 332 (5.23×10^4). HRMS (ESI) m/z : calcd.: 410.9950; found: 410.9964 $[\text{M-PF}_6]^+$. Anal. Calcd. (%) for $\text{C}_{17}\text{H}_{14}\text{ClF}_6\text{N}_4\text{PRu}$: C, 36.74; H, 2.54; N, 10.08. Found (%): C, 36.44; H, 2.84; N, 9.95.

2.3c Complex $[\text{Cp}^*\text{RhL}\kappa^2_{\text{N}\text{O}\text{N}}\text{Cl}]\text{PF}_6$ (3): Yield: (60%). FTIR (KBr pellet, cm^{-1}): 2945 $\nu_{(\text{C-H})}$, 1640 $\nu_{(\text{C=N})}$, 1609 $\nu_{(\text{C=C})}$, 842 $\nu_{(\text{P-F})\text{str}}$, 558 $\nu_{(\text{P-F})\text{ben}}$. ^1H NMR (DMSO- d_6 , 400 MHz, ppm): 9.51 (d, 1H, $J_{\text{HH}} = 8$ Hz), 9.00 (d, 1H, $J_{\text{HH}} = 8$ Hz), 8.78 (d, 1H, $J_{\text{HH}} = 8$ Hz), 8.57 (d, 1H, $J_{\text{HH}} = 8$ Hz), 8.31 (t, 1H, $J_{\text{HH}} = 8$ Hz), 7.96 (t, 1H, $J_{\text{HH}} = 8$ Hz), 7.76 (m, 2H), 1.78 (s, 15H). UV-Vis (MeOH) λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) = 222 (1.29×10^5), 266 (4.51×10^4), 320 (5.1×10^4). HRMS (ESI) m/z calcd.: 469.0666; found: 469.0804 $[\text{M-PF}_6]^+$. Anal. Calcd. (%) for $\text{C}_{21}\text{H}_{23}\text{ClF}_6\text{N}_4\text{PRhC}$, 41.03; H, 3.77; N, 9.11 Found (%): 41.33; H, 3.57; N, 9.31.

2.3d Complex $[\text{Cp}^*\text{IrL}\kappa^2_{\text{N}\text{O}\text{N}}\text{Cl}]\text{PF}_6$ (4): Yield: (42%). FTIR (KBr pellet, cm^{-1}): 2924 $\nu_{(\text{C-H})}$, 1644 $\nu_{(\text{C=N})}$, 1614 $\nu_{(\text{C=C})}$, 844 $\nu_{(\text{P-F})\text{str}}$, 558 $\nu_{(\text{P-F})\text{ben}}$. ^1H NMR (DMSO- d_6 , 400 MHz, δ , ppm): 9.51 (d, 1H, $J_{\text{HH}} = 8$ Hz), 9.02 (d, 1H, $J_{\text{HH}} = 8$ Hz), 8.84 (d, 1H, $J_{\text{HH}} = 8$ Hz), 8.70 (d, 1H, $J_{\text{HH}} = 8$ Hz), 8.33 (t, 1H, $J_{\text{HH}} = 8$ Hz), 8.0 (t, 1H, $J_{\text{HH}} = 8$ Hz), 7.71 (m, 2H), 1.77 (s, 15H). UV-Vis (MeOH) λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) = 221 (8.90×10^4), 287 (6.89×10^4), 333 (5.7×10^4). HRMS (ESI) m/z calcd.: 559.1240; found: 559.1350 $[\text{M-PF}_6]^+$. Anal. Calcd. (%) for $\text{C}_{21}\text{H}_{23}\text{ClF}_6\text{N}_4\text{PIrC}$, 35.82; H, 3.29; N, 7.96 Found (%): 36.05; H, 3.49; N, 8.15.

3. Results and Discussion

3.1 Synthesis

During an attempt to synthesize a Schiff base ligand by condensing *p*-toulenesulphonyl hydrazine with dipyriddy ketone, we observed the formation of an unexpected triazole ligand (Scheme 1). Though the ligand under study is reported by various methods using oxidizing agents, refluxing in methanol with acetic acid is not widely reported. Complexes **1–4** were obtained by treating ligand **L** with the corresponding precursor compound in methanol (Scheme 2). All the complexes were isolated as their hexafluorophosphate salts and were obtained as yellow powders. They are insoluble in chlorinated solvents such as dichloromethane and chloroform, soluble in acetone, alcohols, acetonitrile and dimethyl sulphoxide, soluble in hot water (up to 40°C) and they are insoluble in diethyl ether and hexane.

3.2 Characterization by spectral studies

The IR spectra of the mononuclear complexes **1–4** show the stretching frequencies of C=N, C=C and C-H at around 1640, 1610 and 2925 cm^{-1} , respectively. The formation of ionic complexes with PF_6 counterion is supported by the presence of P-F vibrational stretching frequency at 842–844 cm^{-1} and vibrational bending frequencies at 557–558 cm^{-1} .

The ^1H NMR spectra of complexes **1–4** exhibit signals corresponding to the ligand from 9.65–7.67 ppm

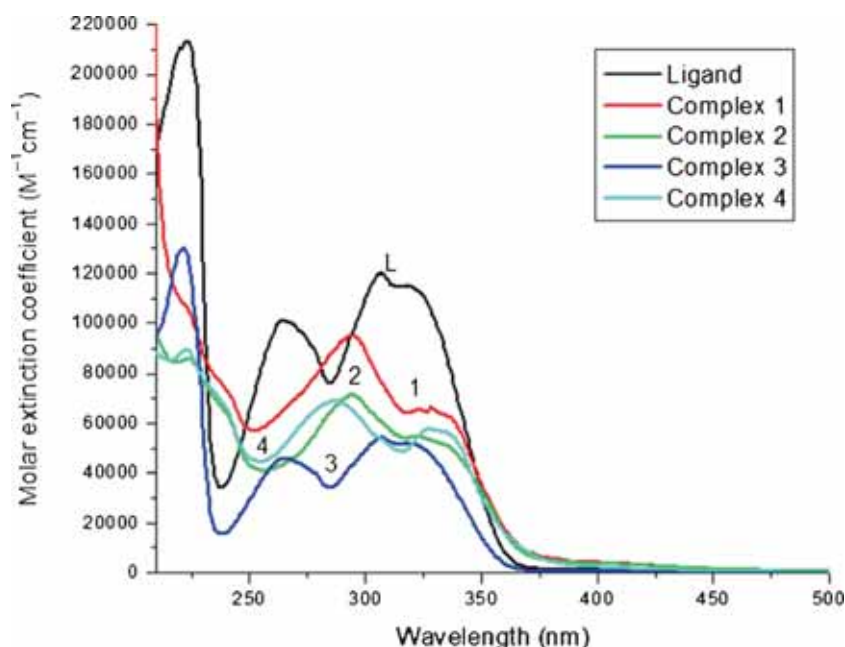


Figure 1. UV-Visible spectra of complexes **1–4** and ligand in methanol at 10 μM concentration.

comprising of doublets, triplets and multiplets corresponding to the two pyridyl rings of the ligand. The ligand in the complexes experiences a downfield chemical shift compared to that of free ligand attributed by the electronegative effect of the metal(s). The presence of the arene metal part is confirmed by the corresponding signals. In complex **1**, two doublets of doublets at 6.20

and 5.99 ppm corresponding to the phenyl ring of the *p*-cymene, a septet at 2.68 ppm, a singlet at 2.13 ppm and a doublet at 1.03 ppm corresponding to the alkyl groups of the *p*-cymene were observed (Figure S1 in Supplementary Information). The presence of a singlet of six protons at 5.56 ppm in complex **2**, a singlet of fifteen protons at 1.78 ppm in complex **3** and

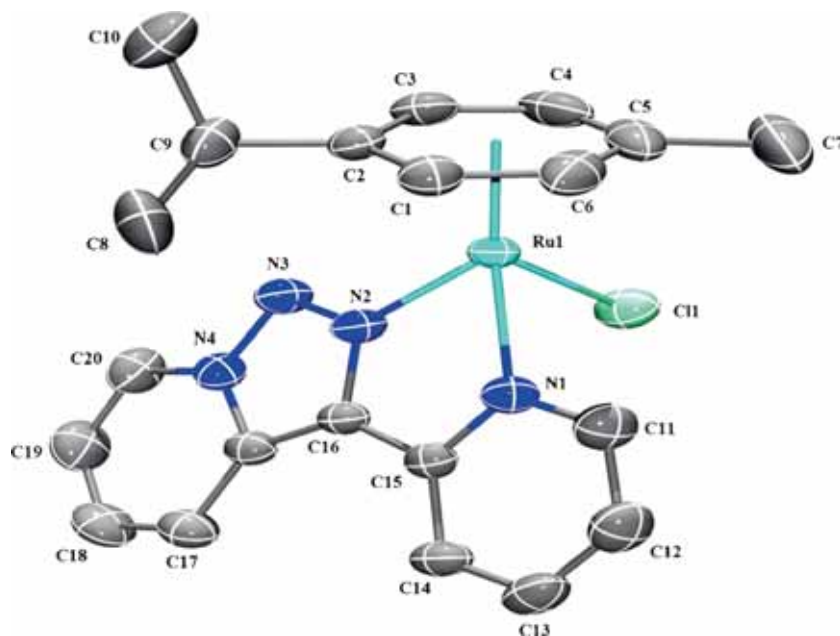


Figure 2. The molecular structure of complex **1** as ORTEP diagram at 50% thermal probability level. Hydrogen atoms and counterions are omitted for clarity.

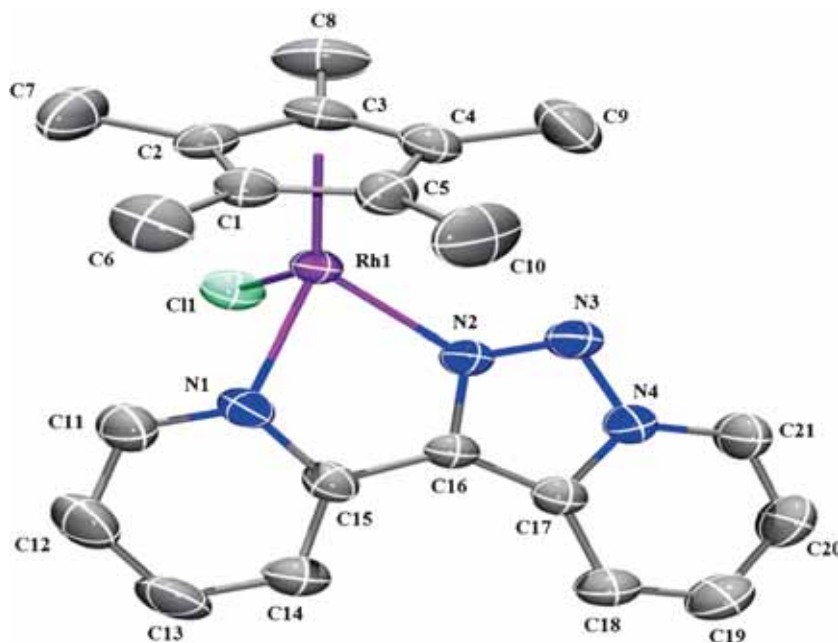


Figure 3. The molecular structure of complex **3** as ORTEP diagram at 50% thermal probability level. Hydrogen atoms and counterions are omitted for clarity.

Table 1. Crystallographic and structure refinement parameters for complexes **1** and **3**.

	1	3
Empirical formula	C ₂₁ H ₂₂ ClF ₆ N ₄ PRu	C ₂₁ H ₂₃ ClN ₄ RhF ₆ P
Formula weight	611.91	614.76
Temperature (K)	273(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic'
Space group	<i>P</i> $\bar{1}$	<i>P</i> 21/ <i>c</i>
Unit cell dimensions (Å, °)		
a	7.2151(4)	8.1467(16)
b	11.9054(7)	12.368(2)
c	14.8743(8)	24.463(5)
α	69.407(5)	90
β	76.898(5)	90
γ	86.939(5)	90
Volume (Å ³), Z	1164.42(12), 2	2464.9(8), 4
Calculated density (mgm ⁻³)	1.745	1.657
Absorption coefficient (mm ⁻¹)	0.922	0.928
Crystal size (mm ³)	0.29 × 0.25 × 0.12	0.31 × 0.21 × 0.21
Scan range	3.681 to 26.372	3.398 to 26.365
Reflections collected	7268	8922
Independent reflections (R _{int})	4868 (0.0343)	49930(0.0194)
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data/restraints/parameters	4866/0/307	4993/0/307
Goodness-of-fit on F ²	1.045	0.749
Final R indices [I > 2 σ (I)]*	R1 = 0.0410, wR2 = 0.1007	R1 = 0.0555, wR2 = 0.0648
R indices (all data)	R1 = 0.0466, wR2 = 0.1038	R1 = 0.1668, wR2 = 0.1784
Largest difference peak and hole (e Å ⁻³)	0.715 and -0.562	1.129 and -1.006

*Structures were refined on F_0^2 : $wR2 = [\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma w(F_0^2)^2]^{1/2}$, where $w^{-1} = [\Sigma(F_0^2) + (aP)^2 + bP]$ and $P = [\max(F_0^2, 0) + 2F_c^2]/3$.

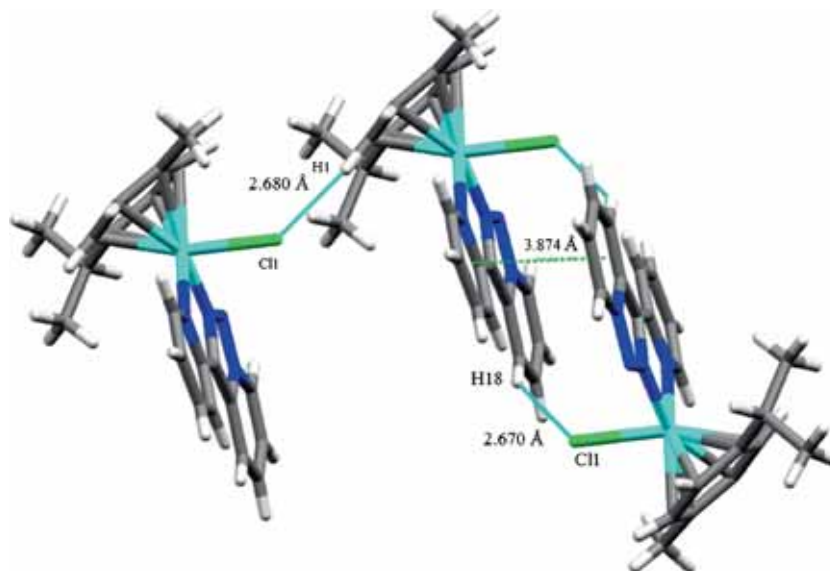
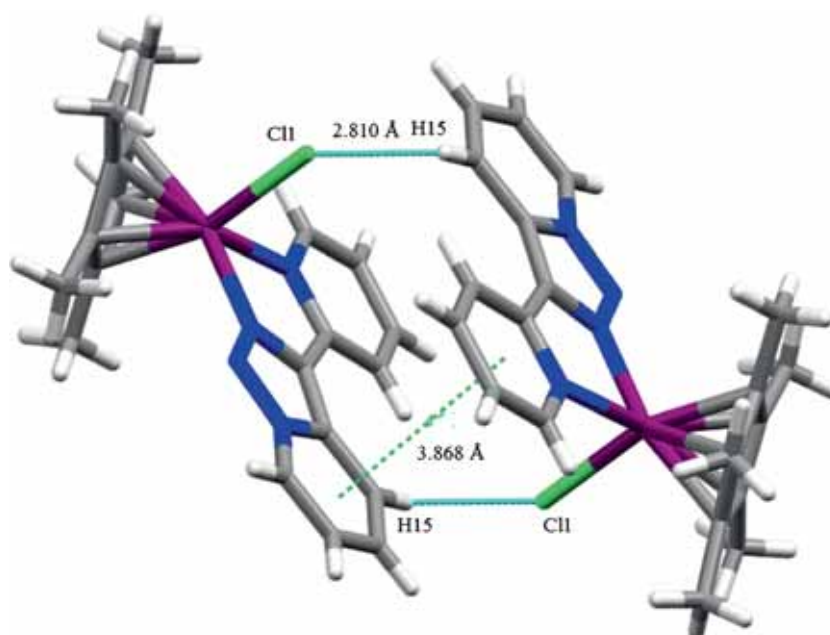
Table 2. Selected bond lengths and angles of complexes **1** and **3**.

Complex	1	3
Bond distances (Å)		
Ru/Rh(1)-Centroid	1.679	1.783
Ru/Rh(1)-Arene _{avg}	2.1911	2.1568
Ru/Rh(1)-N(1)	2.118(3)	2.164(5)
Ru/Rh(1)-N(2)	2.059(3)	2.121(4)
Ru/Rh(1)-Cl(1)	2.3939(10)	2.3913(15)
N(2)-N(3)	1.321(4)	1.317(7)
N(3)-N(4)	1.357(4)	1.374(7)
N(1)-C(11)	1.347(5)	1.332(7)
N(1)-C(15)	1.351(4)	1.377(7)
N(2)-C(16)	1.350(4)	1.359(6)
N(4)-C(17)	1.374(4)	1.377(7)
Bond Angles (°)		
N(1)-Ru/Rh(1)-N(2)	76.21(11)	76.11(15)
N(1)-Ru/Rh(1)-Cl(1)	84.53(8)	87.78(12)
N(2)-Ru/Rh(1)-Cl(1)	85.15(8)	89.88(12)
N(2)-N(3)-N(4)	103.5(3)	104.6(4)
N(3)-N(2)-C(16)	112.8(3)	112.1(4)
N(1)-C(15)-C(16)-N(2)	5.49	0.45

Table 3. Selected hydrogen bond distances (Å) and angles (°) of complexes **1** and **3**.

Complex	D-H...A	D-H(Å)	H...A(Å)	D...A(Å)	<D-H...A(°)
1	C(1)-H(1)...Cl(1) ^a	0.980	2.680	3.642(4)	168
	C(18)-H(18)...Cl(1) ^b	0.930	2.670	3.477(4)	145
3	C(15)-H(15)...Cl(1) ^c	0.930	2.810	3.776(6)	154

*Symmetry axis: a = $-1+x, y, z$. b = $2-x, 1-y, -z$. c = $1-x, -y, -z$.

**Figure 4.** Intermolecular C-H...Cl interactions in complex **1**.**Figure 5.** Intermolecular C-H...Cl interactions in complex **3**.

that at 1.77 ppm in complex **4** confirm the presence of benzene ruthenium, Cp*Rh and Cp*Ir portions of the complexes (Figures S2–S4 in Supplementary Information). Mass spectral study by HRMS has unambiguously confirmed the formation of the complexes. The molecular ion peaks in complexes **1–4** corresponding to the $[M-PF_6]^+$ were found at m/z 467.0604, 410.9964, 469.0804 and 559.1350 respectively (Figures S6–S9 in Supplementary Information). UV-Vis spectra of the ligand and complexes **1–4** were recorded in methanol in 10 μ M solutions. The electronic spectra of these complexes are depicted in (Figure 1). The ligand exhibited three bands at 222, 264 and 306 nm. The electronic spectra of complexes **1–4** display three bands at 221–223 nm, 287–294 nm and 320–334 nm. There is a significant bathochromic shift in the lower energy bands from 264 nm to \sim 290 nm and from 306 to \sim 330 nm.

3.3 Structural studies by X-ray crystallography

The molecular structures of complexes **1** and **3** were confirmed by X-ray structural analyses. The ORTEP drawings with an atom labelling scheme are shown in Figures 2 and 3. The summary of the crystallographic data, bond lengths and angles for these complexes are presented in Tables 1 and 2, respectively. The chelate binding of the ligand and the formation of cationic complexes are explicit in the crystal structures. The metal to centroid distances in complexes **1** and **3** are 1.679 Å and 1.783 Å, respectively, which indicates a longer distance of the arene and metal in the latter case.

In complexes **1** and **3**, metal to nitrogen distances around the metal *viz.*, Ru/Rh-N1/N2 are in the range 2.059 Å to 2.164 Å and the metal chloride distances are 2.393 Å and 2.391 Å, respectively. In the triazole, the N-N distances *viz.*, N2-N3 and N3-N4 in complex **1** are 1.321(4) Å and 1.357(4) Å, respectively, and in complex **3** they are 1.317(7) Å and 1.374(7) Å, respectively, which suggest that the N-N bond attached to pyridine ring is longer than the exocyclic N-N bond which is bound to the metal (Figures 2 and 3). The bite angles around the metal N(1)-Ru/Rh(1)-N(2), N(1)-Ru/Rh(1)-Cl(1) and N(2)-Ru/Rh(1)-Cl(1) are in the range 76.11(15)° to 89.88(12)° which shows a slight deviation from the octahedral geometry resulting in pseudo-octahedral geometry for the complexes. The complexes resemble a “piano stool” with arene occupying the place of the seat and the two nitrogen atoms and chloride as the three legs. The torsion angle at N(1)-C(15)-C(16)-N(2) in complexes **1** and **3** are 5.49° and 0.45° which suggests the existence of more strain around the metal in the ruthenium complex compared to that of rhodium. The packing diagrams of the crystal

structures of the complexes **1** and **3** show the intermolecular C-H \cdots Cl interaction and π – π interaction. In complex **1**, C1-H1 \cdots Cl was observed with 2.680 Å between the donor and acceptor and C(18)-H(18) \cdots Cl(1) was observed with 2.670 Å between the donor and acceptor. In complex **3**, C(15)-H(15) \cdots Cl(1) was observed with 2.810 Å between the donor and acceptor (Figures 4 and 5) (Table 3).

4. Conclusions

In our attempt to synthesize a Schiff base ligand by condensing tosylhydrazine with dipyriddy ketone using glacial acetic acid, we ended up with triazolopyridine by nucleophilic substitution of the tosyl group by pyridyl nitrogen (ligand **L**). All the three metal precursors (M = Ru, Rh and Ir) form mononuclear cationic complexes with the ligand in *N, N*-bidentate chelating mode ($\kappa^2N \cap N$). The metal complexes **1–4** were synthesized and characterized by spectroscopic and crystallographic studies. Complexes under study exhibited a significant bathochromic shift from ligand to complexes in the lower energy region from 264 nm to \sim 290 nm and from 306 to \sim 330 nm. Complexes **1** and **3** exhibited intermolecular C-H \cdots Cl and π – π interactions.

Supplementary Information (SI)

CCDC [1505760] and CCDC [1505761] contain the supplementary crystallographic data for complexes **1** and **3**. 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. ¹H NMR and mass spectra of the corresponding complexes are given in the Supplementary Information, which is available at www.ias.ac.in/chemsci.

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References

1. Kleverlaan C J, Indelli M T, Bignozzi C A, Pavanin L, Scandola F, Hasselman G M and Meyer G J 2000 Stepwise Charge Separation in Heterotriads. Binuclear Ru(II)-Rh(III) Complexes on Nanocrystalline Titanium Dioxide *J. Am. Chem. Soc.* **122** 2840

- Lees A C, Evrard B, Keyes T E, Vos J G, Kleverlaan C J, Alebbi M and Bignozzi C A 1999 Synthesis, Spectroscopy and Photophysical Properties of Ruthenium Triazole Complexes and Their Application as Dye-Molecules in Regenerative Solar Cells *Eur. J. Inorg. Chem.* **12** 2309
- Noyori R and Hashigushi S 1997 Asymmetric Transfer Hydrogenation Catalyzed by Chiral Ruthenium Complexes *Acc. Chem. Res.* **30** 97
- Mayer T J and Huynh M H V 2003 The Remarkable Reactivity of High Oxidation State Ruthenium and Osmium Polypyridyl Complexes *Inorg. Chem.* **42** 8140
- Nakajima H and Nagao Hand Tanaka K 1996 Control of the coordination mode of 1,8-naphthyridine ligated to ruthenium(II) bipyridine complexes *Dalton Trans.* 1405
- Habtemariam M, Melchart R, Fernandez S, Parsons I D H, Oswald A, Parkin F P A, Fabbiani J E, Davidson A, Dawson R E, Aird D I, Jodrell and Sadler P J 2006 Structure-Activity Relationships for Cytotoxic Ruthenium(II) Arene Complexes Containing N,N-, N,O-, and O,O-Chelating Ligands *J. Med. Chem.* **49** 6858
- Melchart M, Habtemariam A, Novakova O, Moggach S A, Fabbiani F P A, Parsons S, Brabec V and Sadler P J 2007 Bifunctional amine-tethered ruthenium(II) arene complexes form monofunctional adducts on DNA *Inorg. Chem.* **46** 8950
- Pandia A K, Ashoka K and Samuelson G 2015 Synthesis and unexpected reactivity of $[\text{Ru}(\eta^6\text{-cymene})\text{Cl}_2(\text{PPh}_2\text{Cl})]$, leading to $[\text{Ru}(\eta^6\text{-cymene})\text{Cl}_2(\text{PPh}_2\text{OH})]$, complexes *J. Chem. Sci.* **127** 1329
- Rakesh K, Rath G and Nagana G 2002 Half-sandwich (η^6 -arene) ruthenium(II) chiral Schiff base complexes: Analysis of the diastereomeric mixtures in solution by 2D-NMR spectroscopy *J. Chem. Sci.* **114** 461
- Hirayama T, Ueda S, Okada T, Tsurue N, Okuda K and Nagasawa H 2014 Facile One-Pot Synthesis of [1,2,3]Triazolo[1,5-*a*]Pyridines from 2-Acylpyridines by Copper(II)-Catalyzed Oxidative N-N Bond Formation *Chem. Eur. J.* **20** 4156
- Niel V, Gaspar A B, Muçoz M C, Abarca B, Ballesteros R and Real J A 2003 Spin crossover behaviour in the iron(II)-2-pyridyl[1,2,3]triazolo[1,5-*a*]pyridine system: X-ray structure, calorimetric, magnetic, and photomagnetic studies *Inorg. Chem.* **42** 4782
- Maury G, Meziane D, Sraïri D, Paugan J P and Paugam R 1982 1,2,3-Triazolo(1,5)Azines et Autres Hétérocycles Azotés Dérivés D'Azine-carboxaldéhydes *Bull. Soc. Chim. Belg.* **91** 153
- Battaglia L P, Carcelli M, Ferraro F, Mavilla L, Pelizzi C and Pelizzi G A 1994 Convenient method for the preparation of 3-(2-pyridyl)triazolo[1,5-*a*]pyridine (L) Crystal structures of L and $[\text{CuL}_2(\text{OH}_2)_2][\text{NO}_3]_2$ *Dalton Trans.* 2651
- Abarca B, Alkorta I, Ballesteros R, Blanco F, Chadlaoui M, Elguero J and Mojarrad F 2005 An experimental and theoretical (DFT) study of the ring chain isomerization *Org. Biomol. Chem.* **3** 3905
- Klinge J, Kaase D, Hilgert J, Steinfeld G, Klingele M H and Lach J 2010 Triazolopyridines as ligands: Structural diversity in iron(II), cobalt(II), nickel(II) and copper(II) complexes of 3-(2-pyridyl)-[1,2,4]triazolo[4,3-*a*]-pyridine and spin crossover in $[\text{Fe}(\text{II})(\text{L})_2(\text{NCS})_2]$ *Dalton Trans.* 4495
- Abarca B, Ballesteros R and Chadlaoui M 2004 Triazolopyridines. Part 24: New polynitrogenated potential helically ligands *Tetrahedron* **60** 5785
- Abarca-Gonzalez B J 2002 The Chemistry of [1,2,3]Triazolo[1,5-*a*]pyridines *Enzyme Inhib. Med. Chem.* **17** 359
- Niel V, Gaspar A B, Munoz M C, Abarca B, Ballesteros R and Real J A 2003 Spin Crossover Behavior in the Iron(II)-2-pyridyl[1,2,3]triazolo[1,5-*a*]pyridine System: X-ray Structure, Calorimetric, Magnetic, and Photomagnetic Studies *Inorg. Chem.* **42** 4782
- Amadei E, Carcelli M, Ianelli S, Cozzini P, Pelagatti P and Pelizzi C 1998 Ligand behaviour and reactivity of phenyl 2-pyridyl ketone azine. Structures of two polymorphic forms of the azine and a copper complex of the 3-phenyltriazolo[1,5-*a*]pyridine *Dalton Trans.* 1025
- Ballesteros R, Abarca B, Samadi A, Server-Carrio J and Escrivá E 1999 Coordinating behaviour of 3-methyl[1,2,3]triazolo[1,5-*a*]pyridine (tzpy): Crystal and molecular structure and electronic properties of $[\text{Cu}(\text{tzpy})_2(\text{ONO}_2)_2(\text{OH}_2)]$ *Polyhedron* **18** 3129
- Richardson C and Steel P J 2002 Metal Complexes of 2-[1,2,3-thia(and seleno)diazolo-4-yl]pyridine and an Unusual Silver-induced Selenadiazole Rearrangement *Aust. J. Chem.* **55** 783
- Fitchett C M, Keene F R, Richardson C and Steel P J 2008 Triazolopyridines. Part 24: New polynitrogenated potential helically ligands *Inorg. Chem. Commun.* **11** 595
- Rao A V, Prasad K T, Wang P and Rao K M 2012 Study of half-sandwich mono and dinuclear complexes of platinum group metals containing pyrazolyl pyridine analogues: Synthesis and spectral characterization *J. Chem. Sci.* **124** 565
- Mahesh K, Forbes S, Mozharivskyj Y and Rao K M 2015 Half-sandwich η^6 -arene ruthenium and Cp* rhodium/iridium compounds comprising with thioether ligands: Synthesis, spectral and molecular studies *J. Chem. Sci.* **127** 1135
- Armarego W L and Chai C L L 2013 In *Purification of laboratory chemicals* (Butterworth-Heinemann: London)
- Bennett M A, Huang T N, Matheson T, Smith A, Ittel S and Nickerson W 2007 (η^6 -Hexamethylbenzene)Ruthenium Complexes *Inorg. Synth.* **21** 74
- White C, Yates A, Maitlis P and Heinekey D 2007 (η^5 -Pentamethylcyclopentadienyl)Rhodium and -Iridium compounds *Inorg. Synth.* **29** 228
- Crysalis PRO, release 2012 Version 1.171.36.20. Agilent Technologies, Yarnton
- Sheldrick G M 2008 *Acta. Crystallogr. A* **64** 112
- Sheldrick G M 2015 *Acta. Crystallogr. C* **71** 3
- Farrugia L J 1997 ORTEP-3 for Windows -a version of ORTEP-III with a Graphical User Interface (GUI) *J. Appl. Crystallogr.* **30** 565
- Bruno I, Cole J, Edgington P, Kessler M, Macrae C F, McCabe P M, Pearson J and Taylor R 2002 New software for searching the Cambridge structural database and visualising crystal structures *Acta Crystallogr. B* **58** 389