Inorganica Chimica Acta 387 (2012) 37–44

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

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

# Novel platinum group metal complexes bearing bidentate chelating pyrimidyl-NHC and pyrimidyl imidazolyl-thione ligands: Syntheses, spectral and structural characterization

Venkateswara Rao Anna [a], Raghavaiah Pallepogu [b], Zhong-Yuan Zhou [c], Mohan Rao Kollipara [a,*]

[a] Department of Chemistry, North-Eastern Hill University, Shillong 793022, India
[b] School of Chemistry, University of Hyderabad, Hyderabad, India
[c] Department of Applied Biology and Chemical Technology, Hong Kong Polytechnic University, Hong Kong, PR China

ARTICLE INFO

*Article history:*
Received 9 November 2011
Received in revised form 22 December 2011
Accepted 23 December 2011
Available online 29 December 2011

*Keywords:*
NHC
Ruthenium
Rhodium
Iridium
1-Pyrimidyl-3-methylimidazolyl bromide

ABSTRACT

A family of novel platinum group metal complexes containing bidentate chelating 1-pyrimidyl-3-methylimidazolyl bromide (**HL1**·**Br**) and 1-pyrimidyl-3-methylimidazolyl-2-thione (**L2**) ligands has been synthesized. The synthetic protocol for the formation of these complexes differs from one ligand to the other. Treatment of ligand (**HL1**·**Br**) with the metal precursors led to the formation of complexes via *in situ* carbene transfer reactions. The silver–NHC complex (**1**) was formed by the reaction of **HL1**·**Br** with silver oxide under light-free conditions. Subsequent addition of appropriate metal precursors to the silver–NHC complex yielded $[(\eta^6\text{-arene})Ru(\mathbf{L1})Cl]PF_6$ complexes {arene = $C_6H_6$ (**2**), *p*-$^{i}PrC_6H_4Me$ (**3**), $C_6Me_6$ (**4**)} on stirring at room temperature, whereas the complexes $[CpRu(\mathbf{L1})(PPh_3)]PF_6$ {Cp = $C_5H_5$ (5), $C_9H_7$ (**6**)} were obtained under reflux conditions. In the case of ligand **L2**, stirring of equimolar quantities of metal precursors and the ligand at room temperature yielded $[(\eta^6\text{-arene})Ru(\mathbf{L2})Cl]PF_6$ {arene = $C_6H_6$ (7), *p*-$^{i}PrC_6H_4Me$ (**8**), $C_6Me_6$ (**9**)}, and $[Cp^*M(\mathbf{L2})Cl]PF_6$ {$Cp^*$ = $C_5Me_5$, M = Rh (**10**), Ir (**11**)}. All these complexes were characterized by CHN analysis, IR, NMR and mass spectrometry besides confirmation by single crystal X-ray diffraction studies for some representative complexes as their hexafluorophosphate salts [**3**]$PF_6$, [**5**]$PF_6$, [**8**]$PF_6$ and [**10**]$PF_6$.



## 1. Introduction

Platinum group metal complexes of stable *N*-heterocyclic carbenes (NHCs) are currently receiving much attention for their wide range of applications in the field of catalysis [1–7]. *N*-heterocyclic carbene ligands can form stable bonds with main group metals as well as with transition metals in various oxidation states due to their strong σ-donating and weak π-accepting character [8]. Some investigations have focused on carbene ligands containing additional functional groups based on donors such as phosphorus, nitrogen, and oxygen. *N*-heterocyclic carbenes having an additional donor group are an important class of ligands for catalysis. The pyridine–NHC ligand combination has received much attention for its utility in transition metal chemistry catalysis and biological applications [9–19]. Many transition metal complexes containing functionalized *N*-heterocyclic carbenes as ligands, display a wide range of applications in organic transformations [20–23]. During recent years, ruthenium–NHC complexes have shown a great potential for the design of new metal-based drugs and biomedical applications [24–26]. Investigations using metal–NHC complexes as catalytic reagents and luminescent emitters [27,28] are becoming prominent currently. Williams first reported the synthesis of bidentate bis-thione ligands ($SS^R$) by reaction of their corresponding imidazolium salts with elemental sulfur in the presence of a base [29,30]. A nickel complex, with a new hard-soft nitrogen-sulfur pyridine–NHC thione ligand, has been shown to assist olefin polymerization [31].

Herein, we report the syntheses and characterization of novel ruthenium-pyrimidine–NHC complexes as well as the syntheses of ruthenium, rhodium and iridium complexes containing the hard-soft nitrogen-sulfur ligand 1-pyrimidyl-3-methylimidazolyl-2-thione (**L2**). The following ligands are used in this study (Chart 1).

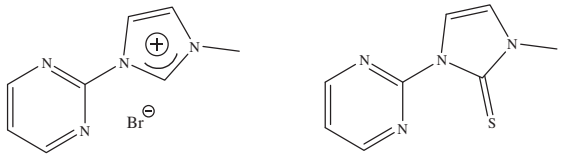
## 2. Results and discussion

### 2.1. Ligand synthesis and characterization

The ligand 1-pyrimidyl-3-methylimidazolyl bromide (**HL1**·**Br**) [32,33] was synthesized by refluxing a mixture of 2-bromopyrimidine with a stoichiometric amount of *N*-methylimidazole in toluene to yield a white solid. The new hard–soft nitrogen–sulfur

* Corresponding author. Tel.: +91 364 272 2620; fax: +91 364 255 0076.
*E-mail address:* mohanrao59@gmail.com (M.R. Kollipara).

0020-1693/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2011.12.048



1-pyrimidyl-3-methylimidazolyl-bromide[HL1·Br] 1-pyrimidyl-3-methylimidazolyl-2-thione[L2]

**Chart 1.** Ligands used in the study.

donor ligand **L2** was readily prepared by deprotonation of **HL1·Br** with potassium *tert*-butoxide (Scheme 1) in THF followed by addition of sulfur at room temperature. The product was purified by flash chromatography using $CH_2Cl_2$ as an eluent. Both the ligands were isolated in moderate yield and characterized by $^1H$ and $^{13}C$ {$^1H$} NMR spectroscopy.

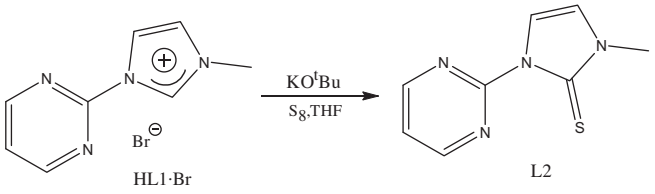
The $^1H$ NMR spectrum of the ligand **HL1·Br** showed two resonances for the pyrimidine ring (a doublet at $\delta$ 8.67 and a triplet at $\delta$ 7.47), while the imidazolyl backbone proton signals were observed in the aromatic region at $\delta$ 8.15 and 7.80. The methyl protons of the imidazolyl ring appeared as a singlet at $\delta$ 2.25, while the acidic NCHN proton signal was observed in the downfield region at $\delta$ 10.6. The $^{13}C$ NMR spectrum of the ligand **HL1·Br** showed resonance for the NCHN carbon at $\delta$ 162.2. The formation of ligand **L2** (Scheme 1) was confirmed by the presence of a singlet at $\delta$ 1.87 along with the two resonances at $\delta$ 6.98 and 7.36 arising from two olefinic (backbone) protons of the imidazolyl moiety. In addition, two doublets ($\delta$ 8.62, 8.68) and one triplet ($\delta$ 7.86) in the aromatic region indicated the presence of pyrimidine ring protons. In the IR spectrum, an intense peak at 1170 $cm^{-1}$ confirmed the presence of the C=S group. Formation of ligand **L2** was further confirmed by the $^{13}C$ NMR spectrum which showed a singlet at $\delta$ 164.60 due to the C=S group.

### 2.2. Synthesis of Ru–NHC complexes

Deprotonation of ligand **HL1·Br** with silver oxide in acetonitrile at room temperature under light-free conditions yielded $[Ag(\mathbf{L1})_2]Br$ (**1**) (Scheme 2). All the Ru–NHC complexes were prepared by *in situ* transmetallation from the silver carbene (**1**) [34]. The dinuclear-arene ruthenium precursor complexes $[(\eta^6\text{-arene})Ru(\mu\text{-Cl})Cl]_2$ reacted with $[Ag(\mathbf{L1})_2]Br$ at room temperature in the presence of $NH_4PF_6$ to form the mononuclear hexafluorophosphate salts of arene ruthenium complexes $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{L1})Cl]^+$ (**2**), $[(\eta^6\text{-}p\text{-}^iPrC_6H_4\text{-}Me)Ru(\mathbf{L1})Cl]^+$ (**3**), and $[(\eta^6\text{-}C_6Me_6)Ru(\mathbf{L1})Cl]^+$ (**4**) (Scheme 3). Similarly, reaction of the complexes $[CpRu(PPh_3)_2Cl]$ and $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ with $[Ag(\mathbf{L1})_2]Br$ in acetonitrile at 80° C led to formation of the mononuclear hexafluorophosphate salts of $[CpRu(\mathbf{L1})(PPh_3)]^+$ (**5**) and $[(\eta^5\text{-}C_9H_7)Ru(\mathbf{L1})(PPh_3)]^+$(**6**) (Scheme 3).

### 2.3. Characterization of Ru–NHC complexes

These complexes were characterized by IR and NMR ($^1H$, $^{13}C$ and $^{31}P$). Analytical data of these complexes corroborated their chemical formulae. The complexes were further confirmed by using mass spectrometry.




**Scheme 1.** Preparation of Ligand 1-pyrimidyl-3-methylimidazolyl-2-thione (**L2**).

The ionic nature of the complexes [**2**–**6**]$PF_6$ was inferred from the IR spectra. A strong band at 840–844 $cm^{-1}$ and a medium band at 550–558 $cm^{-1}$ were assigned to the $\nu_{(P-F)}$ mode of the counter ion, $PF_6^-$.

The absence of acidic imidazolyl NCHN proton resonance at $\delta$ 10.6 confirmed the formation of the Ag–NHC and Ru–NHC complexes. Loss of symmetry of the pyrimidine ring upon coordination to the metal atom was initially inferred from the $^1H$ NMR spectra of complexes [**2**–**6**]$PF_6$ by the conspicuous appearance of three distinct peaks of the pyrimidine ring that were absent in the free imidazolium salt. In the $^1H$ NMR spectra of the complexes [**2**–**4**]$PF_6$, the imidazolyl methyl protons of the ligand exhibited one singlet each at $\delta$ 2.28, 2.26 and 2.29 for the complexes [**2**]$PF_6$, [**3**]$PF_6$ and [**4**]$PF_6$, respectively. In addition to these signals, the arene ligand of the complex [**2**]$PF_6$ showed a singlet for the benzene ring protons at $\delta$ 6.22, while the complex [**4**]$PF_6$ showed a singlet at $\delta$ 2.25 for the hexamethylbenzene ring protons. The $^1H$ NMR spectrum of complex [**3**]$PF_6$ exhibited a singlet at $\delta$ 2.18 for the methyl protons, a septet at $\delta$ 2.69 for the CH proton of the isopropyl group, and two doublets at $\delta$ 1.23 and 1.18 for the diastereotopic methyl protons of the isopropyl group. Moreover, the four doublets, in the range $\delta$ 6.19–5.48, represented the diastereotopic CH protons of the aromatic ring of the *p*-cymene ligand. Since the ruthenium atom is stereogenic due to the coordination of four different ligand atoms onto the metal atom [35–37], such unusual patterns were observed for the diastereotopic methyl protons of the isopropyl group and the aromatic protons of the *p*-cymene ligand. The two imidazolyl backbone protons for the complexes [**2**]$PF_6$, [**3**]$PF_6$ and [**4**]$PF_6$ appeared at $\delta$ 9.59–9.49 and 8.74–8.69 in the proton NMR spectra. In the $^{13}C$ NMR spectra of complexes [**2**]$PF_6$, [**3**]$PF_6$, and [**4**]$PF_6$, the carbenic carbons exhibited relatively downfield shifts at $\delta$ 182.21, 183.41, and 182.91 for the respective carbons in addition to other carbon resonances.

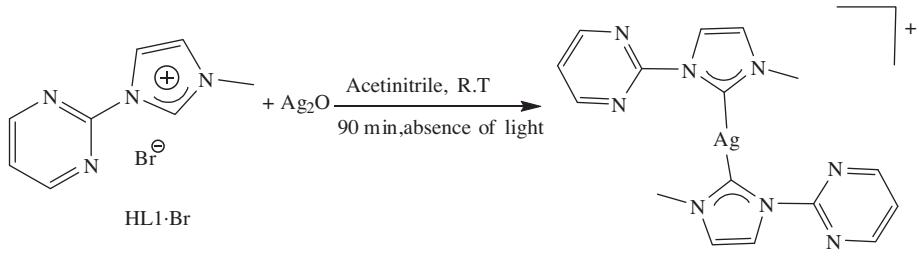
Complex [**5**]$PF_6$ exhibited a singlet at around $\delta$ 5.17 corresponding to the protons of the cyclopentadienyl ligand. The protons of the indenyl group in complex [**6**]$PF_6$ exhibited three sets of characteristic signals, viz., a multiplet, a triplet and a doublet respectively in the regions $\delta$ 8.1–7.12, 5.32 and 4.51. Both the complexes typically exhibited a multiplet in the range $\delta$ 8.10–6.80 indicating the presence of the phosphine and pyrimidine ring protons. The two imidazolyl backbone protons for the complexes [**5**]$PF_6$ and [**6**]$PF_6$ absorbed at $\delta$ 9.59 and 8.90 and at $\delta$ 9.52 and 8.83, respectively.

The formation of the complexes [**5**]$PF_6$ and [**6**]$PF_6$ could be further confirmed through $^{31}P$ NMR. These two complexes exhibited downfield resonances in their $^{31}P$ NMR spectra, at $\delta$ 49.2 and 51.4, which is a feature in contrast to their starting precursors [38,39].

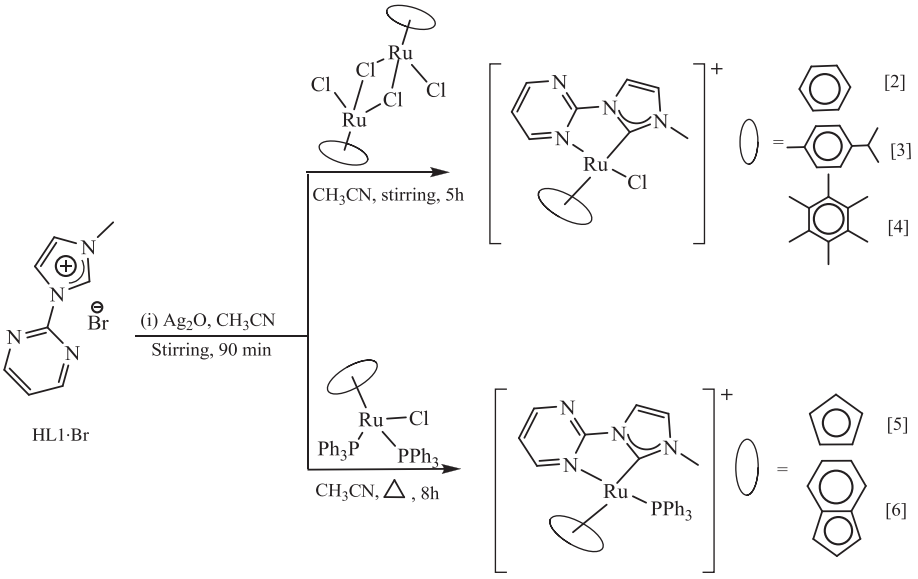
The *m*/*z* values of all the compounds and their stable molecular ion peaks obtained from the mass spectra (listed in Section 3) were in good agreement with the theoretically expected values.

### 2.4. Synthesis of 1-pyrimidyl-methylimidazolyl-thione complexes

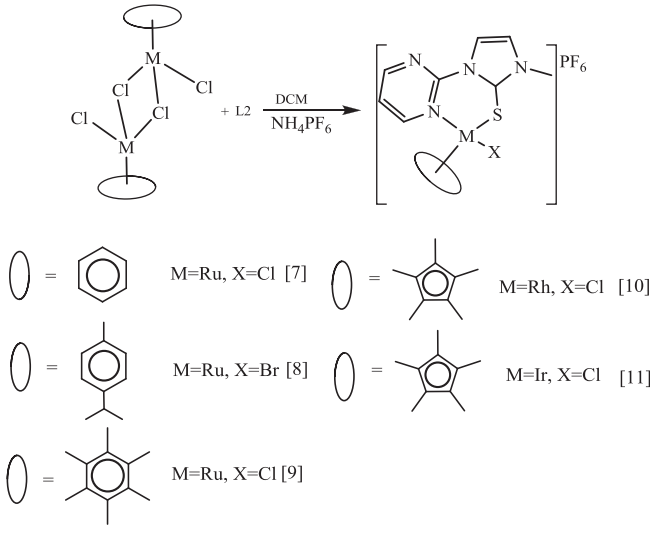
Mononuclear cationic arene/pentamethylcyclopentadienyl metal complexes having the 1-pyrimidyl-3-methylimidazolyl-2-thione [**L2**] ligand, viz., the complexes $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{L2})Cl]PF_6$ or [**7**]$PF_6$, $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(\mathbf{L2})Br]PF_6$ or [**8**]$PF_6$, $[(\eta^6\text{-}C_6Me_6)Ru(\mathbf{L2})Br]PF_6$ or [**9**]$PF_6$, $[Cp^*Rh(\mathbf{L2})Cl]PF_6$ or [**10**]$PF_6$ and $[Cp^*Ir(\mathbf{L2})Cl]PF_6$ or [**11**]$PF_6$ (Scheme 4), were conveniently prepared by the reaction of arene or pentamethylcyclopentadienyl metal complexes $[(\eta^6\text{-arene})Ru(\mu\text{-Cl})Cl]_2$ (arene = $C_6H_6$, *p*-$^iPrC_6H_4Me$ and $C_6Me_6$), and $[Cp^*M(\mu\text{-Cl})Cl]_2$ (M = Rh and Ir) with two equivalents of 1-pyrimidyl-3-methylimidazolyl-2-thione [**L2**] in dichloromethane. These deep-red complexes [**7**–**11**]$PF_6$ were isolated as




**Scheme 2.** Preparation of silver–NHC complex (**1**).




**Scheme 3.** Preparation of arene, cyclopentadienyl and indenyl ruthenium complexes with ligand **L1**.




**Scheme 4.** Preparation of arene and pentamethylcyclopentadienyl complexes with ligand **L2**.

their respective hexafluorophosphate salts. They are non-hygroscopic, air-stable, crystalline solids, and soluble in methanol, dichloromethane, and chloroform. All these complexes were fully characterized by IR, NMR ($^1$H and $^{13}$C). Analytical data of the complexes correlated well with their chemical formulae. Further information about the composition of these complexes was also obtained from mass spectrometry.

### 2.5. Characterization

In the infrared spectra of the ligand 1-pyrimidyl-3-methylimidazolyl-2-thione (**L2**), the absorption bands at 1452 and 1170 cm$^{-1}$ were assigned to the stretching frequencies of C=N and C=S, respectively. Upon coordination with metal atoms, the C=N and C=S bands appeared at around 1449–1458 and 1161–1164 cm$^{-1}$, respectively. In addition to these bands, a strong and a medium band observed in the regions 841–845 and 550–558 cm$^{-1}$, respectively were assigned to the counter ion $PF_6^-$.

The $^1$H NMR spectrum of the free ligand 1-pyrimidyl-3-methylimidazolyl-2-thione (**L2**) exhibited a characteristic set of three resonances for the pyrimidine ring protons and three resonances for the imidazolyl backbone protons and one singlet for the methyl protons. Upon coordination with the metal atom, the six-membered chelating mononuclear cationic complexes [**7**–**11**]$PF_6$ were obtained. Besides these resonances, complexes [**7**]$PF_6$ and [**9**]$PF_6$ exhibited one singlet each at $\delta$ 5.95 and 2.25 for the protons of the benzene and hexamethylbenzene ligands respectively. The complex [**8**]$PF_6$ exhibited a doublet at $\delta$ 1.32 and a septet at $\delta$ 2.70 corresponding to the methyl and methine protons respectively of the isopropyl group. The two doublets observed at $\delta$ 5.81 and 5.56 corresponded to the aromatic *p*-cymene ring protons. The complexes [**10**]$PF_6$ and [**11**]$PF_6$ exhibited strong peaks at $\delta$ 1.89 and 1.85 respectively corresponding to the pentamethylcyclopentadienyl protons, which implied formation of the six-membered monocationic complexes. In the $^1$H NMR spectra, two imidazolyl backbone protons showed two doublets for the complexes [**7**–**11**]$PF_6$ in the ranges $\delta$ 7.51–7.36 and 7.31–7.15,

respectively, whereas the pyrimidine ring protons showed two doublets and a triplet in the ranges $\delta$ 8.86–8.68, 8.74–8.56 and 8.05–7.92, respectively.

### 2.6. Molecular structure presentation

The molecular structures of $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru}(\mathbf{L1})\text{Cl}]^+$ (**3**) $[\text{CpRu}(\mathbf{L1})(\text{PPh}_3)]^+$ (**5**), $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru}(\mathbf{L2})\text{Br}]^+$ (**8**) and $[\text{Cp}^*\text{Rh}(\mathbf{L2})\text{Cl}]^+$ (**10**) {**L1** = 1-pyrimidyl-3-methylimidazol-2-ylidene, **L2** = 1-pyrimidyl-3-methylimidazolyl-2-thione} were established by single-crystal X-ray analyses of their hexafluorophosphate salts shown in Figs. 1–4. All the cationic complexes showed a typical piano-stool geometry with the metal center coordinated to the arene/cyclopentadienyl/pentamethylcyclopentadienyl ligand, a terminal chloride for [**3**]$PF_6$ and [**10**]$PF_6$, a bromide for complex [**8**]$PF_6$ and a triphenylphosphine ligand for complex [**5**]$PF_6$. The metal centers were contained within a pseudo-octahedral coordination mode with the chelating **L1**/**L2** ligand.

The Ru–$C_{carbene}$ bond distances for Ru(II)–NHC complexes [**3**]$PF_6$ and [**5**]$PF_6$ are 2.026 and 2.009 Å, respectively, and hence lie within the expected range of values [40–43]. The centroid distances from metal to arene ring are 1.721, 1.853, 1.659 and 1.787 Å for the complexes [**3**]$PF_6$, [**5**]$PF_6$, [**8**]$PF_6$ and [**10**]$PF_6$, respectively. The five-membered metal chelate-ligand C–Ru–N bite angles are 77.31° for complex [**3**]$PF_6$ and 76.46° for complex [**5**]$PF_6$, while the bite angles for six-membered metal chelate-ligand S–M–N {M = Ru [**8**]$PF_6$, Rh [**10**]$PF_6$} are 85.68° for [**8**]$PF_6$ and 86.35° for [**10**]$PF_6$. In the complexes [**3**]$PF_6$ and [**5**]$PF_6$, the Ru–N coordinate bond distances are 2.074 and 2.099 Å, respectively, which are within the expected range of values [44]. The complex [**3**]$PF_6$ shows a butterfly network viewed along the *c*-axis, as shown in Fig. 5. A number of inter-ionic short C–H···Cl and C–H···F contacts are detected in the crystal structures of [**3**]$PF_6$, [**5**]$PF_6$, [**8**]$PF_6$ and [**10**]$PF_6$, but these are most probably caused by crystal packing effects and should not affect distances and angles in the molecules. The inter-molecular C–H···Cl contacts of the complex [**3**]$PF_6$ are shown in Fig. 6.

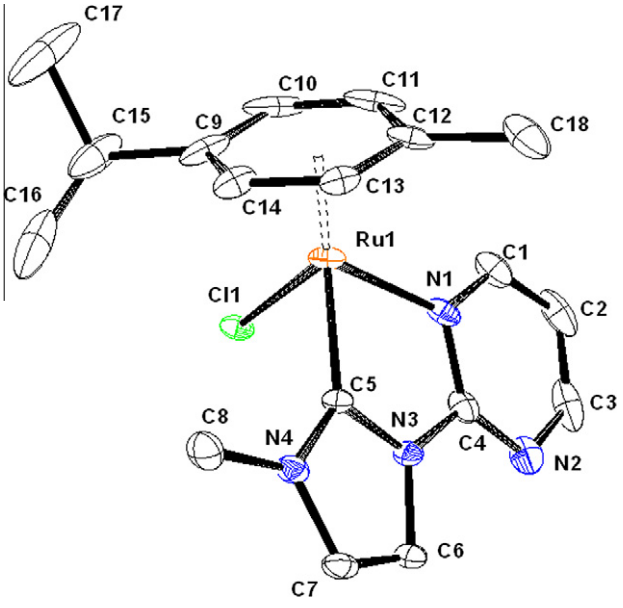



**Fig. 1.** ORTEP drawing of the complex [**3**]$PF_6$. Thermal ellipsoids are shown at 10% probability level with hydrogen atoms and counter ion omitted for clarity. Selected bond distances (Å) and angles (°): Ru(1)-cent. 1.721, Ru(1)–C(5) 2.206(3), Ru(1)–N1 2.704(3), Ru(1)–Cl1 2.4209(7), C(5)–Ru(1)–N1 77.31(10), C(5)–Ru(1)–C13 96.52(10).

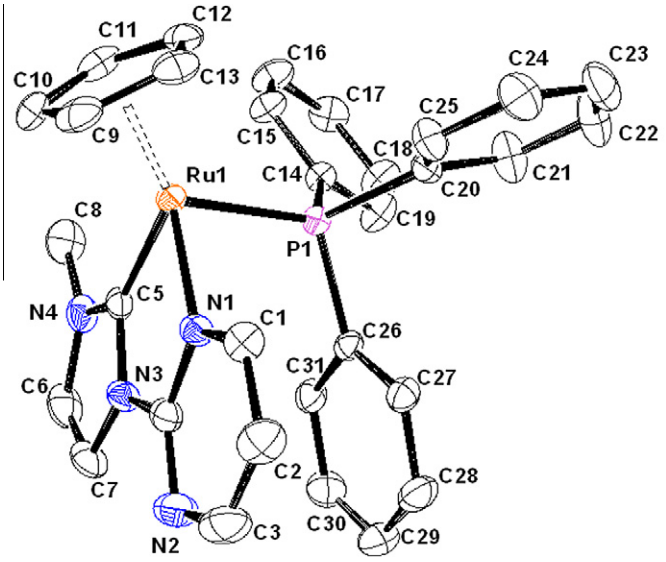



**Fig. 2.** ORTEP drawing of the cationic section of the complex [**5**]$PF_6$. Thermal ellipsoids are shown at 30% probability level with hydrogen atoms and counter ion omitted for clarity. Selected bond distances (Å) and angles (°): Ru(1)-cent. 1.853, Ru(1)–C(5) 2.009(4), Ru(1)–N1 2.099(3), Ru(1)–P1 2.3014(11), C(5)–Ru(1)–N(1) 76.46(15), N(1)–C(4)–N(3) 112.19, C(4)–N(3)–C(5) 119.0(3).

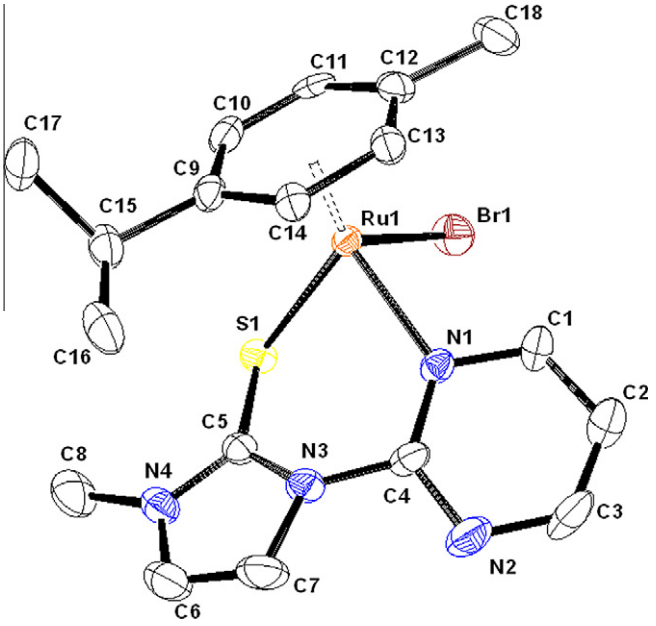



**Fig. 3.** ORTEP drawing of the cationic section of complex [**8**]$PF_6$. Thermal ellipsoids are shown at 30% probability level with hydrogen atoms, chloroform (solvent molecule) and counter ion omitted for clarity. Selected bond distances (Å) and angles (°): Ru(1)–cent. 1.689, Ru(1)–C(5) 2.206(3), Ru(1)–S(1) 2.3933(9), Ru(1)–N1 2.146(3), Ru(1)–Br(1) 2.5181(5), S(1)–Ru(1)–N(1) 85.70(8), N(3)–C(5)–S(1) 127.5(3), N(1)–Ru(1)–Br(1) 115.49(10).

## 3. Experimental

### 3.1. General remarks

All solvents were dried and distilled prior to use. Ruthenium trichloride trihydrate (Arora Matthey Ltd.), *N*-methylimidazole (Aldrich), 2-bromopyrimidine (Aldrich) were purchased and used as received. $[(\eta^6\text{-}C_6H_6)\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$, $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$, $[(\eta^6\text{-}C_6\text{Me}_6)\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$, [44] $[\text{Cp}^*\text{M}(\mu\text{-Cl})\text{Cl}]_2$ (M = Rh, Ir),

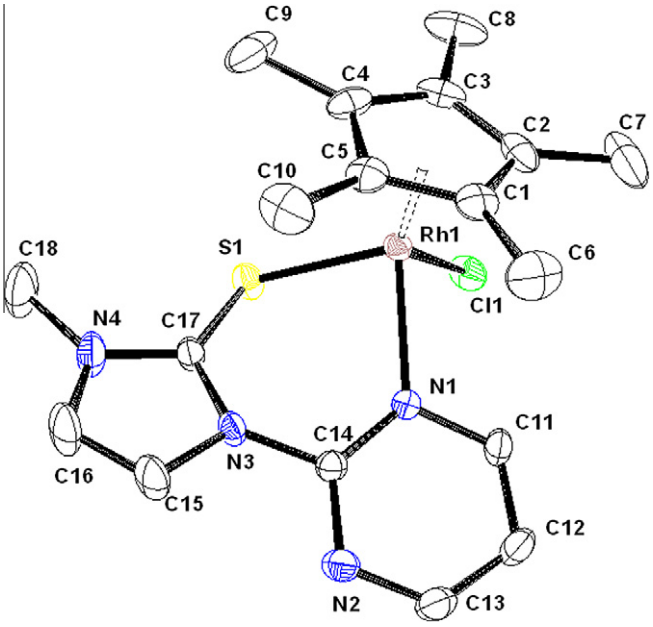



**Fig. 4.** ORTEP drawing of the cationic section of complex [**10**]$PF_6$. Thermal ellipsoids are shown at 30% probability level with hydrogen atoms and counter ion omitted for clarity. Selected bond distances (Å) and angles (°): Rh(1)-cent. 1.787, Rh(1)–S(1) 2.3774(11), Rh(1)–N(1) 2.140(3), Rh(1)–Cl(1) 2.4064(10), N(1)–Rh(1)–S(1) 86.34(9), C(5)–Rh(1)–S(1) 108.42(13), N(1)–Rh(1)–Cl(1) 90.25(9), S(1)–Rh(1)–Cl(1) 86.65(4).

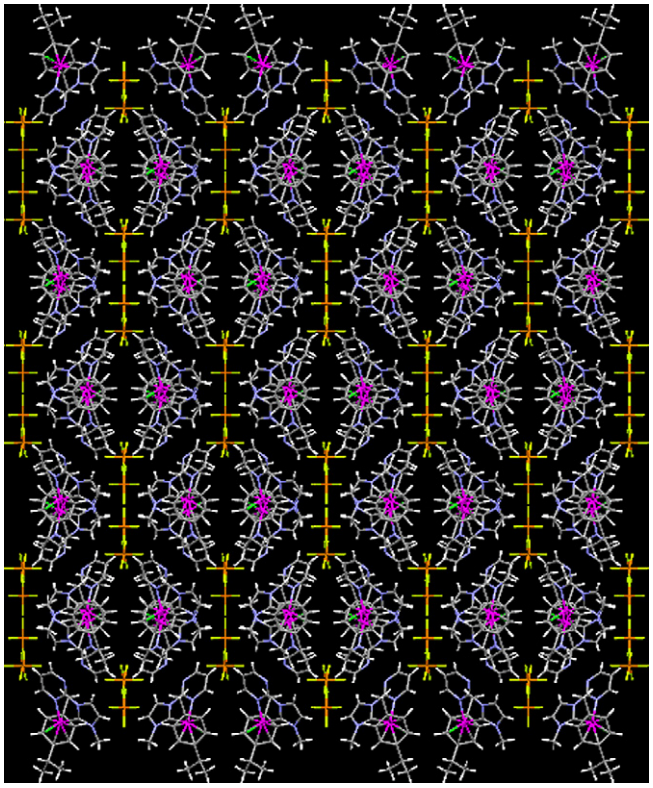


**Fig. 5.** A butterfly network of complex [**3**]$PF_6$ viewed along *c*-axis.

[CpRu($PPh_3$)$_2$Cl] [38], [($\eta^5$-$C_9H_7$)Ru($PPh_3$)$_2$Cl] [39], ligand **HL1·Br** [32,33] and **L2** [31] were prepared according to literature methods. NMR spectra were recorded on a Bruker Avance II 400 MHz spectrometer. Infrared spectra were recorded as KBr pellets on a

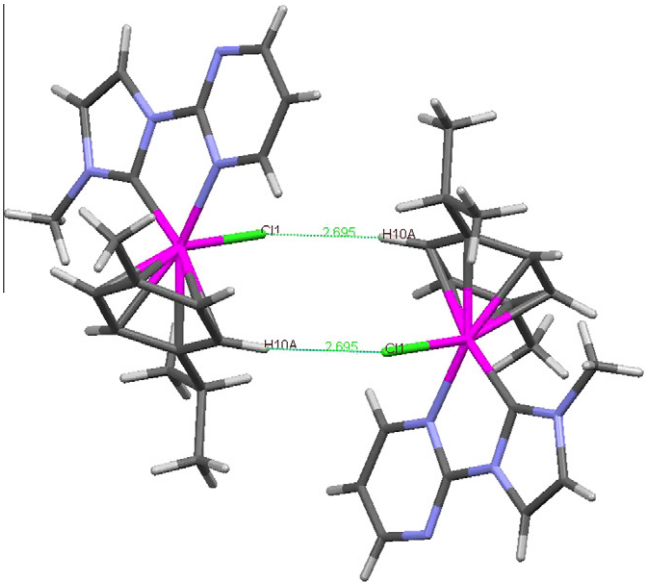



**Fig. 6.** Intermolecular CH. . .Cl interactions of complex [**3**]$PF_6$.

Perkin-Elmer 983 spectrophotometer; elemental analyses of the complexes were performed on a Perkin-Elmer-2400 CHN/S analyzer. Mass spectra were obtained from the LC–MS Waters ZQ-4000 mass spectrometer by the ESI method.

### 3.2. Single-crystal X-ray structure analyses

Molecular structures of the complexes [**3**]$PF_6$, [**5**]$PF_6$, [**8**]$PF_6$·$CHCl_3$ and [**10**]$PF_6$ have been determined by single crystal X-ray diffraction studies. Details about data collection, refinement and structure solution are recorded in Table 1. The ORTEP presentations of the molecular structures with their atom-numbering schemes are shown in Figs. 1–4 along with some selected bond lengths and bond angles. Single-crystal X-ray diffraction data for [**3**]$PF_6$, [**5**]$PF_6$, [**8**]$PF_6$·$CHCl_3$ and [**10**]$PF_6$ were collected on a Bruker Apex II CCD diffractometer with Mo Kα radiation ($\lambda$ = 0.71073 Å) at room temperature. The structures were solved by direct methods using the program SHELXS-97 [45]. Refinement and all further calculations were carried out using SHELXL-97 [45]. The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on $F^2$. Structural illustrations have been drawn with ORTEP-3 [46].

#### 3.2.1. Synthesis of 1-pyrimidyl-3-methylimidazolyl-2-thione [*L2*]

To a solution of 1-pyrimidyl-3-methylimidazolium bromide (0.64 g, 2.62 mmol) in THF (50 ml), potassium *tert*-butoxide (3.00 mmol) was added at room temperature. The mixture was stirred for 10 min and then sulfur (0.096 g, 3.00 mmol) was added. After 15 h, the solution was filtered and the solvent was removed to give a pure product, which was further purified by flash chromatography ($CH_2Cl_2$). Yield: 0.46 g, 75%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.87 (s, $CH_3$, 3H), 6.98 (d, $J$ = 2.92 Hz, 1H, $imid_{backbone}$), 7.36 (d, $J$ = 2.92 Hz, 1H, $imid_{backbone}$), 7.86 (t, 1H, $H_{pyrimidine}$), 8.62 (d, 1H, $H_{pyrimidine}$), 8.68 (d, $J$ = 8.32 Hz, 1H, $H_{pyrimidine}$); $^{13}$C NMR ($CDCl_3$): $\delta$ 28.21 ($CH_3$), 115.32 ($C5_{Im}$), 120.61 ($C4_{Imid}$), 122.72 ($C5_{Pym}$), 137.44 ($C4_{Pym}$), 147.21 ($C2_{Pym}$), 148.51 ($C6_{Pym}$), 164.60 ($C2_{Im}$); IR (KBr, $cm^{-1}$): $\nu_{(C=S)}$ 1170. *Anal.* Calc. for $C_{12}H_{15}N_4S$: C, 61.77; H, 6.48; N, 18.01. Found: C, 61.75; H, 6.47; N, 18.04%.

*3.2.1.1. Complex **1** silver NHC complex.* A solution of **HL1·Br** (100 mg, 0.41 mmol) in $CH_3CN$ (10 ml) was treated with $Ag_2O$

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

| | [**3**]$PF_6$ | [**5**]$PF_6$ | [**8**]$PF_6{\cdot}CHCl_3$ | [**10**]$PF_6$ |
|---|---|---|---|---|
| Chemical formula | $C_{18}H_{22}N_4ClF_6PRu$ | $C_{31}H_{28}N_4F_6P_2Ru$ | $C_{19}H_{23}N_4BrCl_3F_6PRuS$ | $C_{18}H_{23}N_4ClF_6PRhS$ |
| Formula weight | 575.881 | 733.89 | 771.775 | 610.790 |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | $C2/c$ | $P2_1/n$ | $P2_1/n$ | $P2_1/c$ |
| Crystal size ($mm^3$) | $0.24 \times 0.20 \times 0.20$ | $0.22 \times 0.12 \times 0.10$ | $0.36 \times 0.24 \times 0.24$ | $0.32 \times 0.24 \times 0.22$ |
| Crystal color and habit | gold, prism | orange, block | gold, prism | red, block |
| $a$ (Å) | 17.0026(4) | 13.424(3) | 12.3225(4) | 8.3277(8) |
| $b$ (Å) | 18.5679(5) | 14.993(3) | 12.1974(3) | 19.8568(16) |
| $c$ (Å) | 14.2487(4) | 14.903(3) | 18.6323(6) | 14.3019(12) |
| $\beta$ (°) | 98.897(2) | 100.250(3) | 106.934(2) | 94.097(8) |
| $V$ ($Å^3$) | 4444.2(2) | 2951.5(10) | 2679.05(14) | 2358.9(4) |
| $Z$ | 8 | 4 | 4 | 4 |
| $T$ (K) | 296 | 298 | 296 | 293 |
| $D_x$ ($g\,cm^{-3}$) | 1.721 | 1.651 | 1.913 | 1.720 |
| $\mu$ ($mm^{-1}$) | 0.96 | 0.708 | 2.57 | 1.05 |
| $F(000)$ | 2304 | 1480 | 1520 | 1224 |
| $\theta$ Range (°) | 2.1–27.3 | 1.88–26.13 | 2.3–27.2 | 2.66–26.37 |
| Unique reflections | 5004 | 5804 | 6001 | 4815 |
| Reflections used [$I > 2\sigma(I)$] | 2488 | 4663 | 4200 | 3973 |
| $R_{int}$ | 0.062 | 0.057 | 0.054 | 0.032 |
| Final $R$ indices [$I > 2\sigma(I)$]* | $R_1 = 0.0659$, $wR_2 = 0.1772$ | $R_1 = 0.0542$, $wR_2 = 0.1115$ | $R_1 = 0.0776$, $wR_2 = 0.2364$ | $R_1 = 0.0428$, $wR_2 = 0.1084$ |
| $R$ indices (all data) | $R_1 = 0.1328$, $wR_2 = 0.2167$ | $R_1 = 0.0723$, $wR_2 = 0.1187$ | $R_1 = 0.1068$, $wR_2 = 0.2662$ | $R_1 = 0.0543$, $wR_2 = 0.1178$ |
| Goodness-of-fit | 0.999 | 1.068 | 1.004 | 1.037 |
| Maximum, Minimum $\Delta\rho$ ($e\,Å^{-3}$) | 0.847, −0.699 | 1.293, −0.498 | 1.072, −0.982 | 1.082, −0.857 |

(59 mg, 0.25 mmol). The mixture was stirred at room temperature for 90 min with exclusion of light. After filtration through a plug of Celite, the solvent was removed *in vacuo* and the residue washed with ether. Complex **1** was obtained as a white powder. Yield: 105 mg, 72.5%. $^1$H NMR (DMSO-$d_6$): $\delta$ 8.90 (d, $J$ = 4.8 Hz, $H_{pyrimidine}$, 4H), 8.47 (d, $J$ = 2.4 Hz, $imid_{backbone}$, 2H), 7.78 (d, $J$ = 2.4 Hz, $imid_{backbone}$, 2H), 7.65 (t, $J$ = 4.8 Hz, $H_{pyrimidine}$, 2H), 2.34 (s, $CH_3$, 3H); $^{13}$C NMR (DMSO-$d_6$): 184.6 (Ag–C), 165.35, 160.09, 156.51, 124.52, 120.65, 117.42, 32.80; *Anal.* Calc. for $C_{16}H_{18}AgBrN_8$: C, 37.67; H, 3.56; N, 21.97. Found: C, 37.12; H, 3.32; N, 21.25%.

### 3.2.2. Generalized procedure for synthesis of metal complexes [**2**–**4**]$PF_6$

A suspension of the ligand (**HL1**·**Br**) and silver oxide (0.5 equiv) in $CH_3CN$ was stirred at room temperature in the dark for 90 min. The mixture was then filtered through a pad of Celite into the appropriate metal precursor and $NH_4PF_6$ (2.1 equiv) and stirred at room temperature for 5 h. The suspension was filtered through Celite to remove silver salts, and the solvent was removed under reduced pressure. The resulting yellowish-orange solid was washed with ether, dried under vacuum, and recrystallized from $CH_2Cl_2$/hexane.

*3.2.2.1. Complex [**2**]$PF_6$.* Transmetallation was carried out in $CH_3CN$ (10 ml) with **HL1**·**Br** (40 mg, 0.164 mmol), $Ag_2O$ (19 mg, 0.08 mmol), $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl]_2$ (40 mg, 0.08 mmol), and $NH_4PF_6$ (57 mg, 0.34 mmol). The product was isolated as a brown solid. Yield: 60 mg, 70.4%. $^1$H NMR ($CDCl_3$): $\delta$ 9.49 (d, $J$ = 2.4 Hz, 1H, $imid_{backbone}$), 8.61 (d, $J$ = 2.4 Hz, 1H, $imid_{backbone}$), 7.75 (d, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 7.46 (t, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 7.26 (d, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 6.22 (s, 6H, $CH_{arom}$), 2.28 (s, 3H, N–Me); $^{13}$C NMR ($CDCl_3$): $\delta$ 182.21 (imid-C2), 165.24, 160.13, 155.91, 123.92, 119.85, 116.93, 91.10, 36.82; *Anal.* Calc. for $C_{14}H_{14}N_4ClF_6PRu$: C, 37.81; H, 3.17; N, 9.80. Found: C, 37.52; H, 3.03; N, 9.65%. ESI-MS ($m/z$): $[M–PF_6]^+$ = 373.8; IR (KBr, $cm^{-1}$): $\nu_{(P–F)}$ 844 (s), 556 (m).

*3.2.2.2. Complex [**3**]$PF_6$.* Transmetallation was carried out in $CH_3CN$ (10 ml) with **HL1**·**Br** (40 mg, 0.164 mmol), $Ag_2O$ (19 mg, 0.08 mmol), $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(\mu\text{-}Cl)Cl]_2$ (50 mg, 0.08 mmol), and $NH_4PF_6$ (57 mg, 0.34 mmol). The product was isolated as a yellowish-orange solid. Yield: 67.5 mg, 71.8%. $^1$H NMR ($CDCl_3$): $\delta$ 9.56 (d, $J$ = 2.4 Hz, 1H, $imid_{backbone}$), 8.74 (d, $J$ = 2.4 Hz, 1H, $imid_{backbone}$), 7.81 (d, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 7.52 (t, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 7.26 (d, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 6.19 (d, $J$ = 6.1 Hz, 1H, $CH_{p\text{-}cym}$), 6.11 (d, $J$ = 6.0 Hz, 1H, $CH_{p\text{-}cym}$), 5.99 (d, $J$ = 6.1 Hz, 1H, $CH_{p\text{-}cym}$), 5.48 (d, $J$ = 6.1 Hz, 1H, $CH_{p\text{-}cym}$), 2.49 (m, 1H, $CH_{p\text{-}cym\text{-}isopropyl\text{-}H}$), 2.26 (s,3H, N–Me), 2.18 (s, 3H, $H_{p\text{-}cym\text{-}me}$), 1.23 (d, $J$ = 7.2 Hz, 3H, $H_{p\text{-}cym\text{-}me}$), 1.18 (d, $J$ = 7.2 Hz, 3H, $H_{p\text{-}cym\text{-}me}$). $^{13}$C NMR ($CDCl_3$): $\delta$ 183.41 (imid-C2), 165.88, 160.34, 155.92, 128.02, 124.12, 121.15, 117.82, 35.94, 29.25, 23.15, 19.94; *Anal.* Calc. for $C_{18}H_{22}N_4ClF_6PRu$: C, 37.54; H, 3.85; N, 9.73. Found: C, 37.20; H, 3.63; N, 9.51%. ESI-MS ($m/z$): $[M–PF_6]^+$ = 431; IR (KBr, $cm^{-1}$): $\nu_{(P–F)}$ 842 (s), 552 (m).

*3.2.2.3. Complex [**4**]$PF_6$.* Transmetallation was carried out in $CH_3CN$ (10 ml) with **HL1**·**Br** (40 mg, 0.16 mmol), $Ag_2O$ (19 mg, 0.08 mmol), $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}Cl)Cl]_2$ (55 mg, 0.08 mmol), and $NH_4PF_6$ (57 mg, 0.34 mmol). The product was isolated as a deep-red solid. Yield: 74 mg, 74.5%. $^1$H NMR ($CDCl_3$): $\delta$ 9.52 (d, $J$ = 2.4 Hz, 1H, $imid_{backbone}$), 8.74 (d, $J$ = 2.4 Hz, 1H, $imid_{backbone}$), 7.81 (d, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 7.52 (t, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 7.26 (d, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 2.29 (s, 3H, N–Me), 2.25 (s, 18H, $CH_3$); $^{13}$C NMR ($CDCl_3$): $\delta$ 182.91 (imid-C2), 165.68, 160.74, 155.62, 133.02, 124.42, 121.35, 117.62, 36.14, 19.5; *Anal.* Calc. for $C_{20}H_{26}ClN_4F_6PRu$: C, 37.81; H, 3.17; N, 9.80. Found: C, 37.52; H, 3.03; N, 9.65%. ESI-MS ($m/z$): $[M–PF_6]^+$ = 458; IR (KBr, $cm^{-1}$): $\nu_{(P–F)}$ 843 (s), 555 (m).

### 3.2.3. Generalized procedure for synthesis of metal complexes [**5**]$PF_6$ and [**6**]$PF_6$

A suspension of the ligand **HL1**·**Br** and silver oxide (0.5 equiv) in $CH_3CN$ was stirred at room temperature in the dark for 90 min. The mixture was then filtered through a pad of Celite into the appropriate metal precursor and $NH_4PF_6$ (2.1 equiv) and refluxed at 80–85 °C for 8 h. The suspension was filtered through Celite to remove silver salts, and the solvent was removed under reduced pressure. The resulting yellow/deep-red solid was washed with ether, dried under vacuum, and recrystallized from $CH_2Cl_2$/hexane.

*3.2.3.1. Complex [**5**]$PF_6$.* Transmetallation was carried out in $CH_3CN$ (10 ml) **HL1**·**Br** (34 mg, 0.14 mmol), $Ag_2O$ (16 mg, 0.07 mmol),

[$CpRu(PPh_3)_2Cl$] (100 mg, 0.14 mmol) and $NH_4PF_6$ (47.85 mg, 0.29 mmol). The product was isolated as a yellow solid. Yield: 71 mg, 67%. $^1H$ NMR ($CDCl_3$): $\delta$ 9.59 (d, $J$ = 2.4 Hz, 1H, $imid_{backbone}$), 8.90 (d, $J$ = 2.4 Hz, 1H, $imid_{backbone}$), 7.80 (d, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 7.62 (t, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 7.58–6.80 (m, 16H, $PPh_3$ + $H_{pyrimidine}$), 5.17 (s, 5H, $C_5H_5$), 2.28 (s, 3H, N–Me); $^{13}C$ NMR ($CDCl_3$): $\delta$ 184.21, $^{31}P$ {$^1H$} NMR ($CDCl_3$): $\delta$ 49.2; *Anal.* Calc. for $C_{31}H_{28}N_4F_6P_2Ru$: C, 50.75; H, 3.85; N, 7.64. Found: C, 50.58; H, 3.71; N, 7.51%. ESI-MS ($m/z$): $[M–PF_6]^+$ = 588.6; IR (KBr, $cm^{-1}$): $\nu_{(P–F)}$ 843 (s), 558 (m).

*3.2.3.2. Complex [**6**]$PF_6$.* Transmetallation was carried out in $CH_3CN$ (10 ml) with **HL1·Br** (31 mg, 0.128 mmol), $Ag_2O$ (15 mg, 0.06 mmol), [($\eta^5$-$C_9H_7$)$Ru(PPh_3)_2Cl$] (100 mg, 0.13 mmol), and $NH_4PF_6$ (45 mg, 0.27 mmol). The product was isolated as a deep-red solid. Yield: 70 mg, 66.3%. $^1H$ NMR ($CDCl_3$): $\delta$ 9.52 (d, $J$ = 2.4 Hz, 1H, $imid_{backbone}$), 8.83 (d, $J$ = 2.4 Hz, 1H, $imid_{backbone}$), 8.1–6.1 (m, 25H, $PPh_3$ + $H_{pyrimidine}$), 5.32 (t, $J$ = 2 Hz, 1H, $H_{indenyl}$), 4.51 (d, 2H, $H_{indenyl}$), 2.26 (s, 3H, N–Me); $^{13}C$ NMR ($CDCl_3$): $\delta$ 183.90; $^{31}P$ {$^1H$} NMR ($CDCl_3$): $\delta$ 51.4; *Anal.* Calc. for $C_{35}H_{30}N_4F_6P_2Ru$: C, 53.64; H, 3.86; N, 7.15. Found: C, 53.48; H, 3.72; N, 7.01%. ESI-MS ($m/z$): $[M–PF_6]^+$ = 637.6; IR (KBr, $cm^{-1}$): $\nu_{(P–F)}$ 842 (s), 558 (m).

*3.2.4. Generalized procedure for synthesis of metal complexes [**7**]$PF_6$–[**11**]$PF_6$*

A suspension of the ligand **L2**, the appropriate metal precursor and $NH_4PF_6$ (2.1 equiv) was stirred in dichloromethane at room temperature for 12 h. The suspension was filtered through Celite to remove ammonium salts, and the solvent was removed under reduced pressure. The resulting deep-red solid was washed with ether, dried under vacuum, and recrystallized from $CH_2Cl_2$/hexane. Preparation of the complex [**8**]$PF_6$ was carried out *in situ* simultaneously with the ligand preparation. In the complex [**8**]$PF_6$ the terminal chloride was replaced by bromide due to presence of KBr in the ligand. In the preparation of the other complexes, the ligand was first isolated and the complexes then synthesized as per the given procedure.

*3.2.4.1. Complex [**7**]$PF_6$.* A suspension of the ligand **L2** (32 mg, 0.16 mmol), [($\eta^6$-$C_6H_6$)$Ru(\mu$-Cl)Cl]$_2$ (41 mg, 0.08 mmol) and $NH_4PF_6$ (57 mg, 0.34 mmol) was stirred in dichloromethane at room temperature for 12 h. The product was isolated as a deep-red solid. Yield: 62.5 mg, 69%. $^1H$ NMR ($CDCl_3$): $\delta$ 8.68 (d, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 8.56 (d, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 7.92 (t, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 7.36 (d, $J$ = 2.9 Hz, 1H, $imid_{backbone}$), 7.15 (d, $J$ = 2.9 Hz, 1H, $imid_{backbone}$), 5.95 (s, 6H, $C_6H_6$) 1.75 (s, 3H, N–Me); $^{13}C$ NMR ($CDCl_3$): $\delta$ 156.90 (imid-C2), 153.2, 151.52, 138.9, 126.34, 123.2, 121.20, 116.2, 29.12; *Anal.* Calc. for $C_{14}H_{14}N_4ClF_6PRuS$: C, 30.47; H, 2.56; N, 10.15. Found: C, 30.32; H, 2.42; N, 9.92%. ESI-MS ($m/z$): $[M–PF_6]^+$ = 405.9; IR (KBr, $cm^{-1}$): $\nu_{(C=S)}$ 1162, $\nu_{(P–F)}$ 845 (s), 555 (m).

*3.2.4.2. Complex [**8**]$PF_6$.* A suspension of the ligand **L2** (32 mg, 0.16 mmol), [($\eta^6$-*p*-$^iPrC_6H_4Me$)$Ru(\mu$-Cl)Cl]$_2$ (50 mg, 0.08 mmol) and $NH_4PF_6$ (57 mg, 0.34 mmol) was stirred in dichloromethane at room temperature for 12 h. The product was isolated as a deep-red solid. Yield: 65 mg, 65.5%. $^1H$ NMR ($CDCl_3$): $\delta$ 8.75 (d, $J$ = 6.75 Hz, 1H, $H_{pyrimidine}$), 8.62 (d, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 7.99 (t, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), $\delta$ 7.46 (d, $J$ = 3.8 Hz, 1H, $imid_{backbone}$), 7.25 (d, $J$ = 3.8 Hz, 1H, $imid_{backbone}$), 5.81 (d, $J$ = 6.1 Hz, 2H, $CH_{arom}$), 5.56 (d, $J$ = 6.1 Hz, 2H, $CH_{arom}$), 2.70 (m, 1H, $H_{p\text{-}cym}$), 2.1 (s, 3H, $H_{p\text{-}cym\text{-}me}$) 1.69 (s, 3H, N–Me), 1.32 (d, $J$ = 7.2 Hz, 6H, $H_{p\text{-}cym\text{-}me}$); $^{13}C$ NMR ($CDCl_3$): $\delta$ 157.21 (imid-C2), 153.4, 151.13, 144.12, 139.12, 136.12, 123.43, 121.51, 116.39, 92.12, 89.92, 87.65, 83.45, 34.1, 29.67, 23.21, 21.45. *Anal.* Calc. for $C_{18}H_{22}N_4BrF_6PRuS$: C, 33.14; H, 3.40; N, 8.59. Found: C, 32.95; H, 3.29; N, 8.42%. ESI-MS ($m/z$): $[M–PF_6]^+$ = 507.45; IR (KBr, $cm^{-1}$): $\nu_{(C=S)}$ 1164, $\nu_{(P–F)}$ 844 (s), 556 (m).

*3.2.4.3. Complex [**9**]$PF_6$.* A suspension of the ligand **L2** (32 mg, 0.16 mmol), [($\eta^6$-$C_6Me_6$)$Ru(\mu$-Cl)Cl]$_2$ (55 mg, 0.08 mmol) and $NH_4PF_6$ (57 mg, 0.34 mmol) was stirred in dichloromethane at room temperature for 12 h. The product was isolated as a deep-red solid. Yield: 70 mg, 66.9%. $^1H$ NMR ($CDCl_3$): $\delta$ 8.82 (d, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 8.71 (d, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 8.05 (t, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 7.51 (d, $J$ = 3.8 Hz, 1H, $imid_{backbone}$), 7.32 (d, $J$ = 3.8 Hz, 1H, $imid_{backbone}$), 2.25 (s, 18H, $CH_3$), 1.65 (s, 3H, N–Me); $^{13}C$ NMR ($CDCl_3$): $\delta$ 158.52 (imid-C2), 153.54, 151.81, 138.99, 132.34, 123.41, 121.32, 116.45, 29.54, 19.6. *Anal.* Calc. for $C_{20}H_{26}N_4ClF_6PRuS$: C, 37.77; H, 4.12; N, 8.81. Found: C, 37.30; H, 4.02; N, 8.56%. ESI-MS ($m/z$): $[M–PF_6]^+$ = 490; IR (KBr, $cm^{-1}$): $\nu_{(C=S)}$ 1161, $\nu_{(P–F)}$ 843 (s), 555 (m).

*3.2.4.4. Complex [**10**]$PF_6$.* A suspension of the ligand **L2** (31.15 mg, 0.16 mmol), [$Cp^*Rh(\mu$-Cl)Cl]$_2$ (50 mg, 0.081 mmol) and $NH_4PF_6$ (56.2 mg,0.32 mmol) was stirred in dichloromethane at room temperature for 12 h. The product was isolated as a deep-red solid. Yield: 72.5 mg, 73.4%. $^1H$ NMR ($CDCl_3$): $\delta$ 8.79 (d, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 8.62 (d, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 7.99 (t, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 7.42 (d, $J$ = 3.8 Hz, 1H, $imid_{backbone}$), 7.26 (d, $J$ = 3.8 Hz, 1H, $imid_{backbone}$), 1.89 (s,15H, $C_5Me_5$), 1.62 (s,3H, N–Me); $^{13}C$ NMR ($CDCl_3$): $\delta$ 158.12 (imid-C2), 152.98, 151.32, 138.12, 132.13, 123.21, 121.22, 116.15, 29.67, 12.96; *Anal.* Calc. for $C_{18}H_{23}N_4ClF_6PRhS$: C, 35.40; H, 3.80; N, 9.17. Found: C, 35.05; H, 3.62; N, 8.99%. ESI-MS ($m/z$): $[M–PF_6]^+$ = 464.8; IR (KBr, $cm^{-1}$): $\nu_{(C=S)}$ 1164, $\nu_{(P–F)}$ 843 (s), 552 (m).

*3.2.4.5. Complex [**11**]$PF_6$.* A suspension of the ligand **L2** (31 mg, 0.16 mmol), [$Cp^*Ir(\mu$-Cl)Cl]$_2$ (65 mg, 0.08 mmol) and $NH_4PF_6$ (56 mg, 0.32 mmol) was stirred in dichloromethane at room temperature for 12 h. The product was isolated as a deep-red solid. Yield: 80 mg, 70.5%. $^1H$ NMR ($CDCl_3$): $\delta$ 8.86 (d, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 8.74 (d, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), 8.04 (t, $J$ = 4.8 Hz, 1H, $H_{pyrimidine}$), $\delta$ 7.51 (d, $J$ = 3.8 Hz, 1H, $imid_{backbone}$), 7.31 (d, $J$ = 3.8 Hz, 1H, $imid_{backbone}$), 1.89 (s,15H, $C_5Me_5$), 1.65 (s,3H, N–Me); $^{13}C$ NMR ($CDCl_3$): $\delta$ 158.45 (imid-C2), 153.06, 151.65, 138.24, 132.18, 123.29, 121.45, 116.19, 29.63, 12.88. *Anal.* Calc. for $C_{18}H_{23}N_4ClF_6PIrS$: C, 30.88; H, 3.31; N, 8.00. Found: C, 30.55; H, 3.18; N, 7.82%; ESI-MS ($m/z$): $[M–PF_6]^+$ = 554.1; IR (KBr, $cm^{-1}$): $\nu_{(C=S)}$ 1163, $\nu_{(P–F)}$ 842 (s), 551 (m).

## 4. Conclusions

In conclusion, the arene, cyclopentadienyl and indenyl Ru(II) mononuclear complexes containing pyrimidine functionalized NHC ligand have been synthesized via *in situ* carbene transfer reactions and structurally characterized. We have chosen these Ru–NHC complexes to perform some application orientation studies though not discussed here. The potential of the Ru–NHC complexes in organic transformations and water oxidation catalysis is under investigation. We have reported the synthesis of new ligand 1-pyrimidyl-3-methylimidazolyl-2-thione. For the first time we reported the syntheses of mononuclear arene Ru(II)/pentamethylcyclopentadienyl Rh(III) and Ir(III) complexes bearing hard–soft nitrogen–sulfur donor ligand 1-pyrimidyl-3-methylimidazolyl-2-thione.

## Acknowledgements

The authors thank *CSIR*, *New Delhi* for providing the financial support in the form of financial Grant Sanction No. 01(2493)/11/EMR-II and for research fellowship (UGC-RFSMS). Thanks are due to Prof. R.H. Duncan Lyngdoh for help in preparing the manuscript.

## Appendix A. Supplementary material

CCDC 832458 ([**3**]$PF_6$), 832459 ([**5**]$PF_6$), 832460 ([**8**]$PF_6{\cdot}CHCl_3$) and 832457 ([**10**]$PF_6$) contain the supplementary crystallographic data for this paper. 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 online version, at doi:10.1016/j.ica.2011.12.048.

## References

[1] A.A.D. Tulloch, A.A. Danopoulos, S. Winston, S. Kleinhenz, G. Eastham, J. Chem. Soc., Dalton Trans. (2000) 4499.
[2] S. Gründemann, A. Kovacevic, M. Albrecht, J.W. Faller, R.H. Crabtree, J. Am. Chem. Soc. 124 (2002) 10473.
[3] E. Colacino, J. Martinez, F. Lamaty, Coord. Chem. Rev. 251 (2007) 726.
[4] E. Assen, B. Kantchev, C.J. O'Brien, M.G. Organ, Angew. Chem., Int. Ed. 46 (2007) 2768.
[5] E.M. Prokopchuk, R.J. Puddephatt, Organometallics 22 (2003) 563.
[6] T.N. Tekavec, J. Louie, Top. Organomet. Chem. 21 (2007) 159.
[7] X. Wang, S. Liu, G.X. Jin, Organometallics 23 (2004) 6002.
[8] D.A. Dixon, A.J. Arduengo III, J. Phys. Chem. 95 (1991) 4180.
[9] J.C.C. Chen, I.J.B. Lin, Organometallics 19 (2000) 5113.
[10] A.A. Danopoulos, A.A.D. Tulloch, S. Winston, G. Eastham, M.B. Hursthouse, Dalton Trans. (2003) 1009.
[11] R.S. Simons, P. Custer, C.A. Tessier, W.J. Youngs, Organometallics 22 (2003) 1979.
[12] S.U. Son, K.H. Park, Y.S. Lee, B.Y. Kim, C.H. Choi, M.S. Lah, Y.H. Jang, Du-J. Jang, Y.K. Chung, Inorg. Chem. 43 (2004) 6896.
[13] S. Gründemann, M. Albrecht, J.A. Loch, J.W. Faller, R.H. Crabtree, Organometallics 20 (2001) 5485.
[14] D.J. Nielsen, K.J. Cavell, B.W. Skelton, A.H. White, Inorg. Chim. Acta 327 (2002) 116.
[15] M. Poyatos, J.A. Mata, E. Falomir, R.H. Crabtree, E. Peris, Organometallics 22 (2003) 1110.
[16] D.S. McGuinness, V.C. Gibson, J.W. Steed, Organometallics 23 (2004) 6288.
[17] A. Melaiye, R.S. Simons, A. Milsted, F. Pingitore, C. Wesdemiotis, C.A. Tessier, W.J. Youngs, J. Med. Chem. 47 (2004) 973.
[18] W.A. Herrmann, Angew. Chem., Int. Ed. 41 (2002) 1290.
[19] A.T. Normand, K.J. Cavell, Eur. J. Inorg. Chem. (2008) 2781.
[20] H.M. Lee, C.-C. Lee, P.-Y. Cheng, Curr. Org. Chem. 11 (2007) 1491.
[21] W.A. Herrmann, M. Elison, J. Fischer, C. Köcher, G.R.J. Artus, Angew. Chem., Int. Ed. Engl. 34 (1995) 2371.
[22] Diez-Gonzalez, N. Marion, S.P. Nolan, Chem. Rev. 109 (2009) 3612.
[23] F.E. Hahn, M.C. Jahnke, Angew. Chem., Int. Ed. 47 (2008) 3122.
[24] J.M. Alfaro, A. Prades, M.D. Carmen Ramos, E. Peris, J. Ripoll-Gomez, M. Poyatos, J.S. Burgos, Zebrafish 7 (2010) 13.
[25] A. Kascatan-Nebioglu, A. Melaiye, K. Hindi, S. Durmus, M.J. Panzner, L.A. Hogue, R.J. Mallett, C.E. Hovis, M. Coughenour, S.D. Crosby, A. Milsted, D.L. Ely, C.A. Tessier, C.L. Cannon, W.J. Youngs, J. Med. Chem. 49 (2006) 6811.
[26] A. Melaiye, Z.H. Sun, K. Hindi, A. Milsted, D. Ely, D.H. Reneker, C.A. Tessier, W.J. Youngs, J. Am. Chem. Soc. 127 (2005) 2285.
[27] S.U. Son, K.H. Park, Y.-S. Lee, B.Y. Kim, C.H. Choi, M.S. Lah, Y.H. Jang, D.-J. Jang, Y.K. Chung, Inorg. Chem. 43 (2004) 6896.
[28] T. Sajoto, P.I. Djurovich, A. Tamayo, M. Yousufuddin, R. Bau, M.E. Thompson, R.J. Holmes, S.R. Forrest, Inorg. Chem. 44 (2005) 7992.
[29] D.J. Williams, D. Vanderveer, R.L. Jones, D.S. Menaldino, Inorg. Chim. Acta 165 (1989) 173.
[30] D.J. Williams, A. Shilatifard, D. Vanderveer, L.A. Lipscomb, R.L. Jones, Inorg. Chim. Acta 202 (1992) 53.
[31] Yuan-Biao Huang, Wei-Guo Jia, Guo-Xin Jin, J. Organomet. Chem. 694 (2009) 86.
[32] J. Ye, W. Chen, D. Wang, Dalton Trans. (2008) 4015.
[33] X. Zhang, B. Liu, A. Liu, W. Xie, W. Chen, Organometallics 28 (2009) 1336.
[34] D. Gnanamgari, E.L.O. Sauer, N.D. Schley, C. Butler, C.D. Incarvito, R.H. Crabtree, Organometallics 28 (2009) 321.
[35] D.L. Davies, O.A. Duaij, J. Fawcett, M. Giardiello, S.T. Hilton, D.R. Russell, Dalton Trans. (2003) 4132.
[36] R. Lalrempuia, K.M. Rao, P.J. Carroll, Polyhedron 22 (2003) 605.
[37] K.T. Prasad, B. Therrien, K.M. Rao, J. Organomet. Chem. 693 (2008) 3049.
[38] M.I. Bruce, N.J. Windsor, Aust. J. Chem. 30 (1977) 1601.
[39] L.A. Oro, M.A. Ciriano, M. Campo, C. Foces-Foces, F.H. Cano, J. Organomet. Chem. 289 (1985) 117.
[40] Y. Tanabe, F. Hanasaka, K. Fujita, R. Yamaguchi, Organometallics 26 (2007) 4618.
[41] R. Corberan, M. Sanau, E. Peris, J. Am. Chem. Soc. 128 (2006) 3974.
[42] F. Hanasaka, K. Fujita, R. Yamaguchi, Organometallics 24 (2005) 3422.
[43] F. Hanasaka, K. Fujita, R. Yamaguchi, Organometallics 23 (2004) 1490.
[44] M.A. Bennett, T.–N. Huang, T.W. Matheson, A.K. Smith, Inorg. Synth. 21 (1982) 74.
[45] G.M. Sheldrick, SHELXL-97 and SHELXS-97, Program for X-ray Crystal Structure Refinement and Solution, Universität Göttingen, Germany, 1997.
[46] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.