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Ruthenium half-sandwich complexes with tautomerized pyrazolyl-pyridazine ligands: Synthesis, spectroscopic and molecular structural studies

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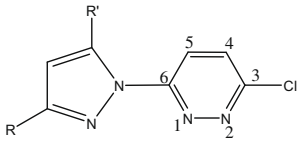
ABSTRACT

Condensation of 1,4-dichloropyridazine with pyrazole, 3,5-dimethylpyrazole and 3-methylpyrazole yielded two types of pyrazolyl-pyridazine ligands, *viz*., (i) products of substitution on one side of the pyridazine as 3-chloro-6-(pyrazolyl)pyridazine (Cl–L1), 3-chloro-6-(3,5-dimethylpyrazolyl)pyridazine (Cl–L2) and 3-chloro-6-(3-methylpyrazolyl)pyridazine (Cl–L3), and (ii) products of substitution on both sides such as 3,6-bis(pyrazolyl)pyridazine (L1), 3,6-bis(3,5-dimethylpyrazolyl)pyridazine (L2) and *tautomers* of 3,6-bis(3-methylpyrazolyl)pyridazine (L3). The reactions of η^6-areneruthenium complexes in methanol with the above mentioned pyrazolyl-pyridazine ligands form mononuclear complexes of the type $[(\eta^6\text{-arene})Ru(Cl\text{–}L)(Cl)]^+$ and $[(\eta^6\text{-arene})Ru(L)(Cl)]^+$; (arene = benzene and *p*-cymene; Cl–L = Cl–L1, Cl–L2, Cl–L3; L = L1, L2, L3). All these complexes are characterized by IR, NMR, mass spectrometry and UV–vis spectroscopy. The structures of some representative complexes are established by single crystal X-ray diffraction studies.

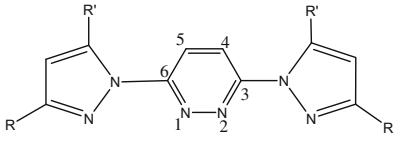
1. Introduction

Arene metal complexes have been extensively investigated by organometallic and organic chemists for over 40 years. In particular, η^6-arene metal complexes have emerged as versatile intermediates in organic synthesis as a consequence of the ease with which the arene ligand can be functionalized [1,2]. Coordination of a metal fragment to an arene ring dramatically facilitates electrophilic aromatic addition and substitution, arene deprotonation, and benzylic deprotonation. Arene metal complexes have been utilized as homogeneous catalysts or catalyst precursors in numerous transformations such as hydrogenation, esterification, olefin metathesis and Diels–Alder cycloaddition [3–6]. In recent years, we have been carrying out reactions of arene ruthenium dimers with a variety of nitrogen-based ligands [7–12] including pyridyl-pyridazine and pyrazolyl-pyradazine ligands. Ruthenium complexes of these types of nitrogen-based ligands have a capacity to function as catalysts for the oxidation of water to oxygen [13,14]. Although extensive studies have been made on ruthenium complexes containing polypyridyl ligands, complexes containing annular tautomerized pyrazolyl-pyradazine ligands have not yet been investigated.

Herein, we describe the synthesis of pyrazole-based ligands in which the starting 3-methylpyrazole moiety tautomerizes to a 5-methylpyrazole moiety [15]; the existence of both tautomers in a single compound is reported here. The syntheses of 12 mononuclear arene ruthenium complexes incorporating these as well as some other pyrazolyl-pyridazine ligands are also reported. Given below are the structures of the ligands used in this study. All these complexes are characterized by IR, NMR, mass spectrometry and UV–vis spectroscopy. The molecular structures of the ligand (L3) and four representative complexes are also presented in this paper.



R=R'=H, Cl-L1 (3-chloro-6-(pyrazolyl)pyridazine)
R=R'=CH_3, Cl-L2 (3-chloro-6-(3,5-dimethylpyrazolyl)pyridazine)
R=CH_3, R'=H, Cl-L3 (3-chloro-6-(3-methylpyrazolyl)pyridazine)



R=R'=H, L1 (3,6-Bis(pyrazolyl)pyridazine)
R=R'=CH_3, L2 (3,6-Bis(3,5-dimethylpyrazolyl)pyridazine)
R=CH_3, R'=H, L3 (3,6-Bis(3-methylpyrazolyl)pyridazine)

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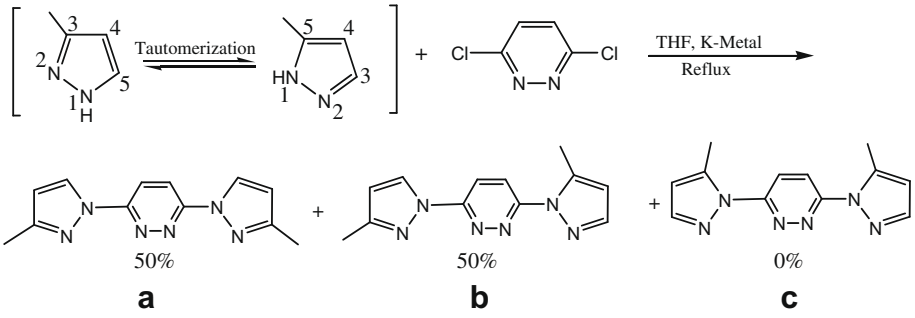
2. Results and discussion

2.1. Pyrazolyl-pyridazine ligands

The ligands were synthesized by a known procedure [16] involving the condensation of 3,6-dichloropyridazine with substituted pyrazoles by refluxing in THF for around 8 h. These starting materials in 1:1 ratio yielded one-side condensation products, *viz*., pyrazolylchloropyridazines, while in 1:2 ratios they yielded both-side condensation products such as bis-pyrazolylpyridazines. In the case of both-side condensation, a small fraction of the one-side condensed product is also formed which is easily separated. An interesting phenomenon observed here is that, in the preparation of the ligand 3,6-bis(3-methylpyrazolyl)pyridazine (L3), a 1:1 mixture of two isomers, *viz*., 3,6-bis(3-methylpyrazolyl)pyridazine and 6-(3-methylpyrazolyl)-3-(5-methylpyrazolyl)pyridazine is formed. The presence of both isomers was confirmed by ^{13}C NMR spectroscopy. Apparently the starting 3-methylpyrazole under the reaction conditions undergoes tautomerization as shown in Scheme 1.

The existence of the two annular tautomers is reported herein. The numbering of the pyrazole carbons depends on the concerned tautomer, since the protonated nitrogen (N–H) is always N1. In the tautomer A (Scheme 1) [17], C3 is the carbon bearing the methyl substituent, while in B it is C5. The isomer ratios are determined tentatively by taking the ^{13}C NMR spectrum of a concentrated solution of the synthesized ligand (L3) in $CDCl_3$ (see Fig. 1). The isomers are not easily separable by TLC or column chromatography. Crystallization yielded single crystals of the 3,3-isomer of the pyrazolyl-pyridazine ligand (L3) whose crystal structure is presented herein. However, after metallation, the presence of both the 3,3- and 3,5-pyrazolyl-pyridazine tautomers is confirmed from the combination of single crystal X-ray structure of the complex [**11**]ClO_4, as well as from the ^{13}C NMR spectrum of the ligand and the complex. We were able to isolate single crystals of the 3,3-isomer of the ligand and of the complex containing the 3,5-isomer of the ligand, indicating both isomers exist in the pure ligand as well as in the complex. The ^{13}C NMR spectrum of the ligand in $CDCl_3$ reveals that the signal at 13.8 ppm corresponds to 3-methylpyrazole (≈50%), whereas the signal at 14.8 ppm is for 5-methylpyrazole (≈50%) (Fig. 1). Although the formation of another isomer, *viz*., 3,6-bis(5-methylpyrazolyl)pyridazine is also hypothetically possible (C in Scheme 1), its formation here was not observed from these NMR studies.



Scheme 1.

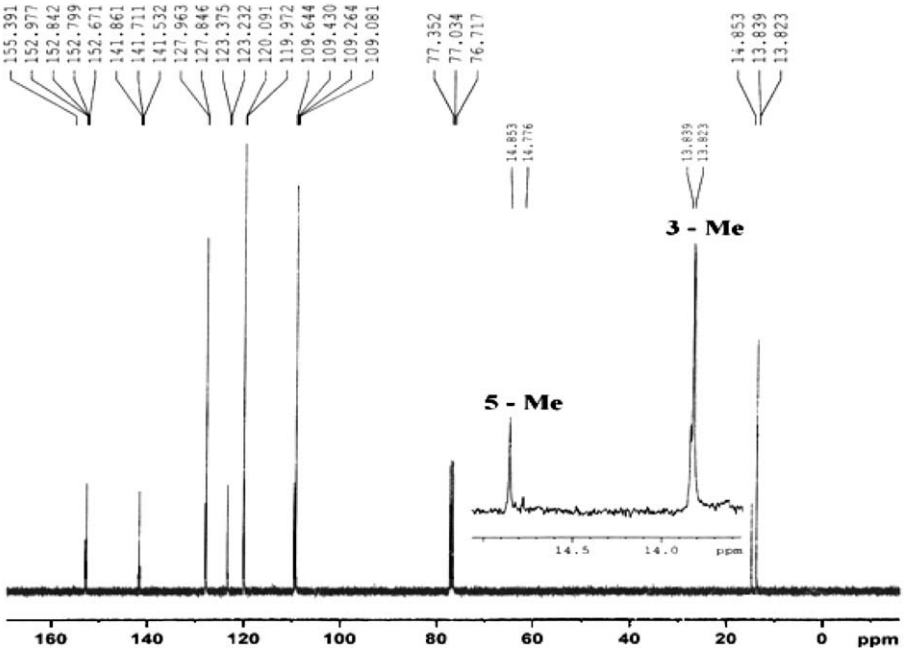


Fig. 1. ^{13}C NMR spectrum of the 3,3/3,5-mixture of ligand **L3** in $CDCl_3$.

2.2. Arene ruthenium complexes

The dinuclear arene ruthenium complexes $[(\eta^6\text{-arene})Ru(\mu\text{-Cl})Cl]_2$ (arene = C_6H_6, *p*-cymene) reacted in methanol with the ligands (Cl–L1), (Cl–L2), (Cl–L3), L1, L2 and L3 to give the mononuclear cationic complexes $[(\eta^6\text{-}p\text{-cymene})Ru(L)Cl]^+$ {L = Cl–L1 ([**1**]PF_6); Cl–L2 ([**3**]PF_6); Cl–L3 ([**5**]PF_6); L1 ([**7**]PF_6); L2 ([**9**]PF_6); L3 ([**11**]ClO_4) and $[(\eta^6\text{-}C_6H_6)Ru(L)Cl]^+$ {L = Cl–L1 ([**2**]PF_6); Cl–L2 ([**4**]PF_6); Cl–L3 ([**6**]PF_6); L1 ([**8**]PF_6); L2 ([**10**]PF_6); L3 ([**12**]PF_6)} (Schemes 2 and 3). The cationic ruthenium complexes ([**1**]PF_6) to ([**10**]PF_6) and ([**12**]PF_6) are obtained as their hexafluorophosphate salts, while complex ([**11**]ClO_4) is obtained as its perchlorate salt.

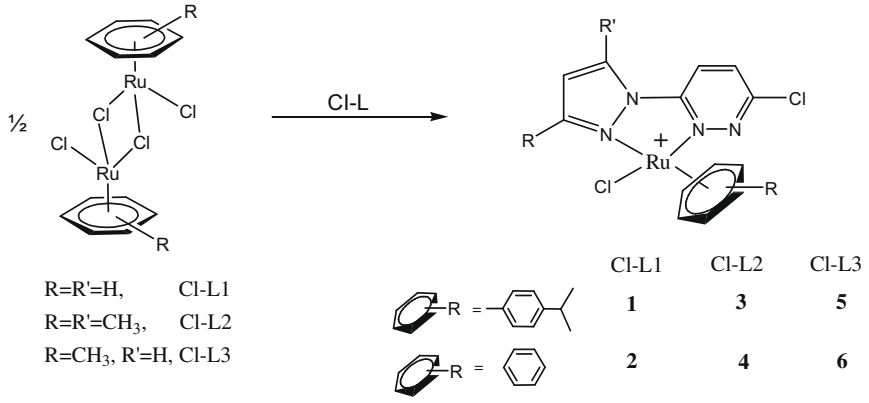
The complexes ([**1**]PF_6, [**3**]PF_6, [**5**]PF_6, [**7**]PF_6, [**9**]PF_6 and [**11**]ClO_4) are yellow in color, while the complexes ([**2**]PF_6, [**4**]PF_6, [**6**]PF_6, [**8**]PF_6, [**10**]PF_6 and [**12**]PF_6) are yellowish-brown in color. They are non-hygroscopic, air-stable solids. The complexes ([**1**]PF_6, [**3**]PF_6, [**5**]PF_6, [**7**]PF_6, [**9**]PF_6 and [**11**]ClO_4) are soluble in solvents like acetonitrile, methanol, dichloromethane, chloroform, acetone, *etc*., but insoluble in hexane, petroleum ether and diethyl ether. The complexes {[**2**]PF_6, [**4**]PF_6, [**6**]PF_6, [**8**]PF_6, [**10**]PF_6 and [**12**]PF_6} are soluble in acetonitrile and partially soluble in dichloromethane, chloroform, methanol and acetone.

The infrared spectra of these complexes exhibit a strong $\nu_{C=N}$ band in the range of 1543–1583 cm^{-1} and a $\nu_{C=C}$ band in the range of 1437–1450 cm^{-1} which are the characteristic bands of the ligands. Besides these, the complexes ([**1**]PF_6 to [**10**]PF_6 and [**12**]PF_6) also exhibit a strong band at around 836–845 cm^{-1} due to the stretching ν_{P-F} mode of the counter ion of these complexes. However, in the case of the complex [**11**]ClO_4, a strong absorption at 1100 cm^{-1} is observed due to the perchlorate ion [18]. The *m*/*z* values of all these complexes and their stable ion peaks obtained from the ZQ mass spectra, as listed in the experimental section, are in good agreement with the theoretically expected values.

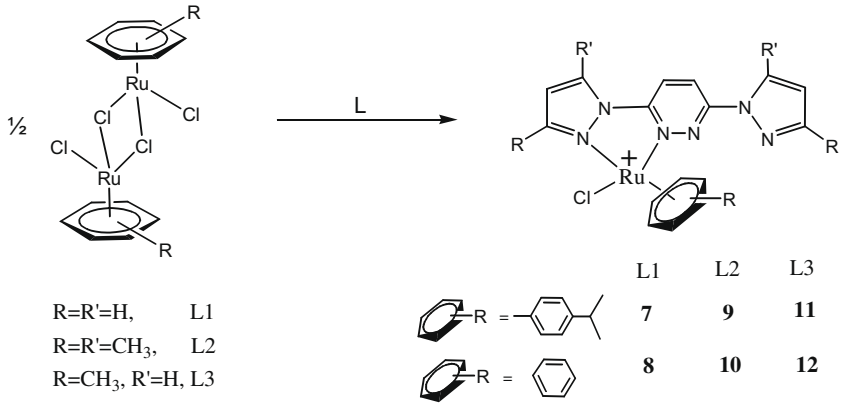
2.3. NMR spectroscopy

The ^1H NMR spectra of the *p*-cymene and benzene derivatives which have Cl–L1, Cl–L2, Cl–L3, L1, L2 and L3 as ligands exhibit three resonances in the region δ = 8.02–6.39 for Cl–L1 ([**1**]PF_6, [**2**]PF_6), three resonances in the region δ = 8.05–6.40 for Cl–L2 ([**3**]PF_6, [**4**]PF_6), four resonances in the region δ = 8.58–7.92 for Cl–L3 ([**5**]PF_6, [**6**]PF_6), eight resonances at around δ = 8.72–6.48 for L1 ([**7**]PF_6, [**8**]PF_6), three resonances at around δ = 8.50–6.54 for L2 ([**9**]PF_6, [**10**]PF_6) and six resonances in the region δ = 8.53–6.34 for L3 ([**11**]ClO_4, [**12**]PF_6) in the aromatic region corresponding to the pyrazole and pyridazine protons which are clearly assigned as shown later. Besides these, all ligands other than Cl–L1 and L1 show a singlet in the region δ = 2.70–2.20 which corresponds to the methyl protons of these ligands.

The ^{13}C NMR spectrum of the complex [**11**]ClO_4 (Fig. 2) indicates a mixture of the two tautomers of the ligand. We were unable to separate these isomers. However, we were able to provide assignments of the resonances for both isomers. Crystallization yields the tautomer of the 3,5-complex (see molecular structure). The peaks assigned at around 13.6 and 14.3 ppm correspond, respectively, to the methyl carbons of the 3,3-isomer and of the 3,5-isomer of the ligand, which are also in accordance with the methyl peaks of the isomers as shown in ^{13}C NMR spectrum of the free ligands (Fig. 1). This also confirms the presence of both the tautomers in the complex as well.



Scheme 2.



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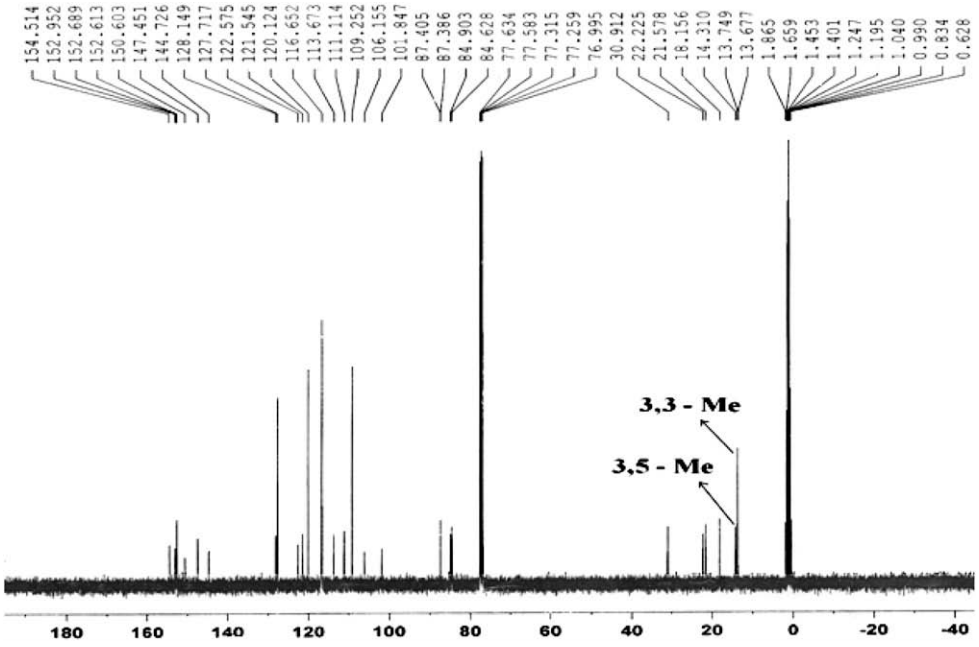

Fig. 2. ^{13}C NMR spectrum of the 3,3/3,5-mixture of complex [**11**]ClO_4 in $CDCl_3$ + CD_3CN.

In addition to these signals, complexes [**2**]PF_6, [**4**]PF_6, [**6**]PF_6, [**8**]PF_6, [**10**]PF_6 and [**12**]PF_6 exhibit a singlet for the benzene ring protons at $\delta = 6.25$–6.04. The complexes [**1**]PF_6, [**3**]PF_6, [**5**]PF_6, [**7**]PF_6, [**9**]PF_6 and [**11**]ClO_4 exhibit an unusual pattern of resonances for the *p*-cymene ligand. For instance, the methyl protons

Table 1
UV–vis absorption data in acetonitrile at 298 K.

Complex		λ_{max}/nm ($\varepsilon/10^{-4}$ M^{-1} cm^{-1})	
[**1**]PF_6	335(0.25)	412(0.14)	
[**2**]PF_6	302(0.20)	340(0.07)	410(0.04)
[**3**]PF_6	292(0.60)	365(0.17)	420(0.14)
[**4**]PF_6	360(0.09)	415(0.06)	
[**9**]PF_6	305(0.90)	368(0.14)	418(0.07)
[**11**]ClO_4	293(0.99)	366(0.05)	413(0.04)
[**12**]PF_6	302(0.46)	365(0.05)	414(0.04)

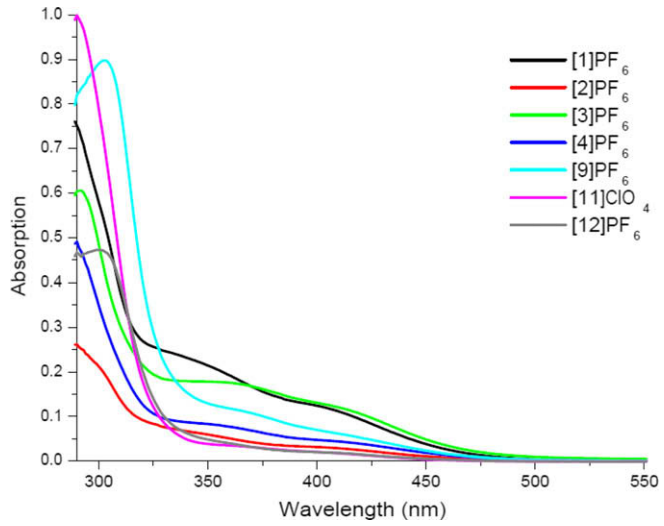

Fig. 3. UV–vis spectra of complexes [**1**]PF_6 to [**4**]PF_6, [**9**]PF_6, [**11**]ClO_4 and [**12**]PF_6 in acetonitrile at 298 K.

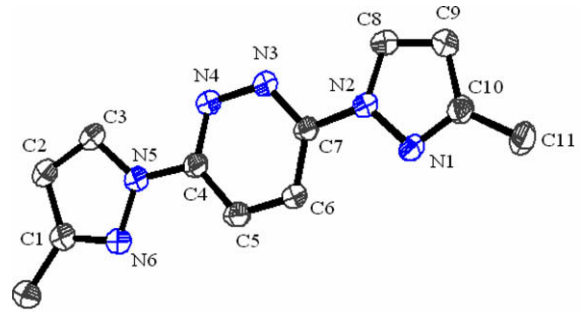

Fig. 4. Molecular structure of the ligand L3 with 50% probability thermal ellipsoids.

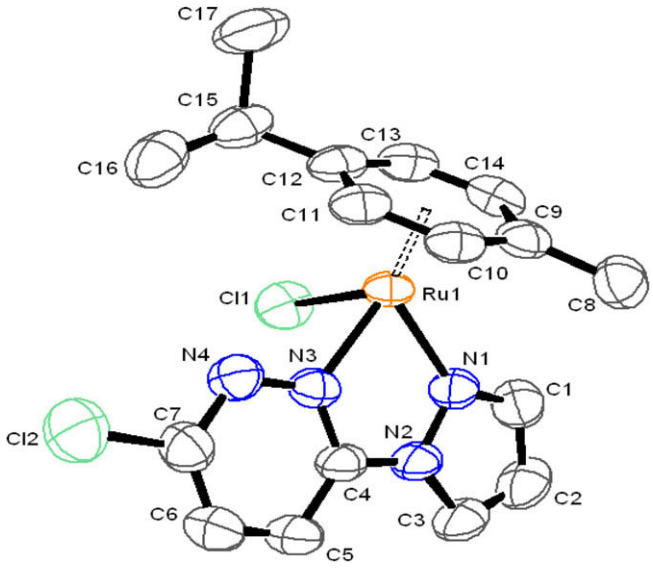

Fig. 5. Molecular structure of complex [(η^6-*p*-cymene)Ru(Cl–L1)Cl]PF_6 [**1**]PF_6 with 50% probability thermal ellipsoids.

of the isopropyl group display two doublets at *ca.* δ = 1.53–1.08, instead of one doublet as in the starting precursor. The aromatic protons of the *p*-cymene ligand for these complexes also display four doublets at *ca.* δ = 6.20–5.68, instead of two doublets as in the starting precursor. This pattern is due to the diastereotopic nature of the methyl protons of the isopropyl group and the aromatic protons of the *p*-cymene ligand. It may also be attributed to the behavior of the ruthenium atom which is stereogenic when coordinated with four different ligand atoms [19]. In other words we can say the different signals are entirely due to the chiral nature of the metal [20,21].

2.4. UV–vis spectroscopy

UV–vis spectra of the complexes [**1**]PF_6 to [**4**]PF_6, [**9**]PF_6, [**11**]ClO_4 and [**12**]PF_6 were acquired in acetonitrile and spectral data are summarized in Table 1. Electronic spectra of representative complexes are depicted in Fig. 3. The low spin d^6 configuration of these mononuclear complexes provides filled orbitals of proper symmetry at the Ru(II) centers which can interact with the low lying π^* orbital of the ligands. One should therefore expect a band attributable to the metal-to-ligand charge transfer (MLCT) $t_{2g} \rightarrow \pi^*$ transition in their electronic spectra [22–27]. The electronic spectra of these complexes display a medium intensity band in the UV–vis region. The lowest energy absorption bands in the electronic spectra of these complexes in the visible region ~420–410 and ~368–335 nm have been tentatively assigned on the basis of their intensity and position to $\pi \rightarrow \pi^*$ MLCT transitions. The bands on the high energy side at ~305–292 nm for the complexes [**2**]PF_6, [**3**]PF_6, [**9**]PF_6, [**11**]ClO_4 and [**12**]PF_6, have been assigned to ligand-centered $\pi \rightarrow \pi^*/n \rightarrow \pi^*$ transitions [28,29]. In general, these complexes follow the normal trends observed in the electronic spectra of the nitrogen-bonded metal complexes, which display a ligand-based $\pi \rightarrow \pi^*$ transition for pyrazolyl-pyridazine ligands in the UV region and metal-to-ligand charge transfer transitions in the visible region.

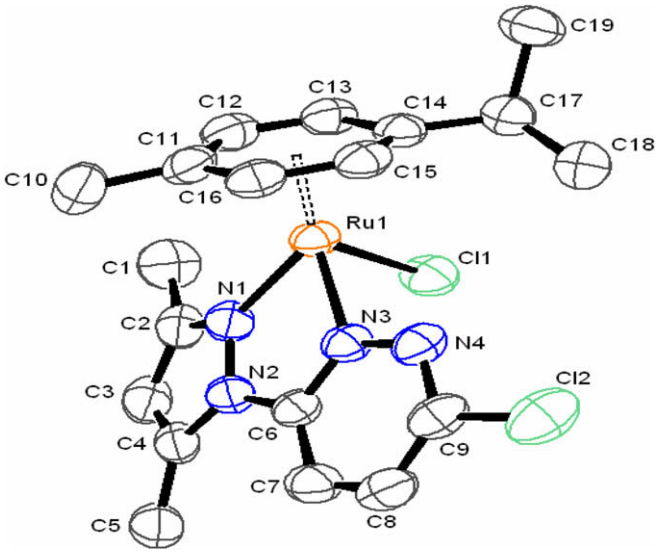

Fig. 6. Molecular structure of complex [(η^6-*p*-cymene)Ru(Cl–L2)Cl]PF_6 [**3**]PF_6 with 50% probability thermal ellipsoids.

2.5. Molecular structures

The crystal structures of the ligand **L3** and the complexes [**1**]PF_6, [**3**]PF_6, [**10**]PF_6 and [**11**]ClO_4 are shown in Figs. 4–8, respectively. Selected inter-atomic distances and angles are listed in Table 2. The overall geometry of all these structures [except **L3**] corresponds to the characteristic piano-stool configuration. For all these compounds, the aromatic ring is planar as observed in related structures [30,31]. The aromatic C–H bonds are bent umbrella-like towards the metal. We also observe a significant alternation in the aromatic C–C distances. The N1–Ru bond length in complex [**11**]ClO_4 is shorter by 0.029 Å than the N1–Ru average bond distance in complexes [**1**]PF_6 and [**3**]PF_6. The Ru–Cl bond distance of all these complexes are almost similar to those of other Ru–Cl complexes reported [32–40]. The N–N bond distances in all the complexes and in the ligand are comparable to each other, *i.e.*, not much variation is observed. The average P–F bond distance is 1.553(4) Å. The average metal–centroid distance is 1.685 Å, which appears to be close to the average distance of 1.69 Å in other Ru(II)–Cl complexes [41].

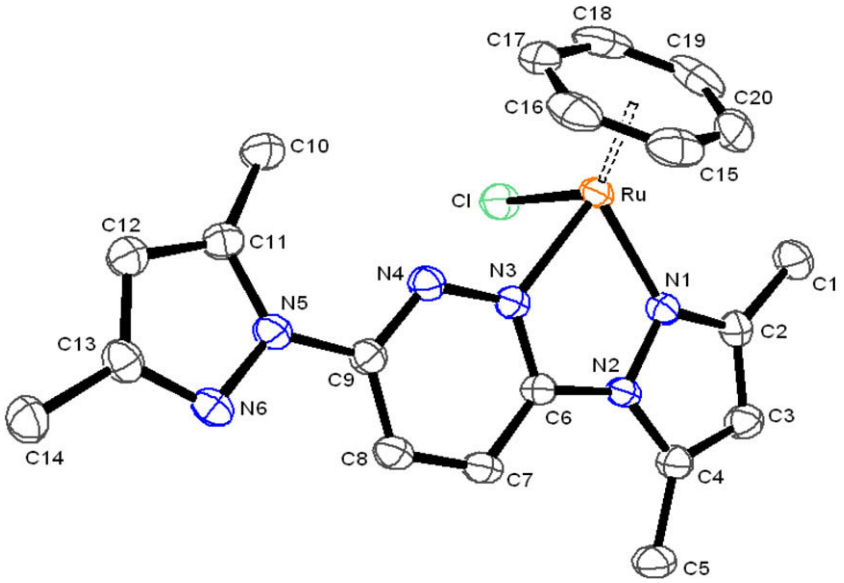

Fig. 7. Molecular structure of complex [(η^6-C_6H_6)Ru(L2)Cl]PF_6 [**10**]PF_6 with 50% probability thermal ellipsoids.

Values of the angle N1–Ru–N3 in the *p*-cymene complexes [**3**]PF_6, [**10**]PF_6 and [**11**]ClO_4 are, respectively, 75.38(14)°, 75.50(9)° and 75.9(2)°, while in the benzene complex [**1**]PF_6 the value is 76.09(14)°, larger than for the *p*-cymene complexes. In contrast, the angle Ru–N(1)–N(2) for the benzene complex [**1**]PF_6 is smaller than for the *p*-cymene complexes [**3**]PF_6, [**10**]PF_6 and [**11**]ClO_4. The *p*-cymene hydrogens and the pyrazole hydrogen of one molecule and the pyrazole hydrogens of another molecule are involved in an intermolecular C–H···O interaction with oxygen atoms of the ClO_4 counter ion (Fig. 9). The matrices for these interactions are as follows: H1···O2 (2.503 Å), H4A···O4 (2.594 Å), H22A···O2 (2.705 Å) and ∠H1–O2–H22A (76.25°).

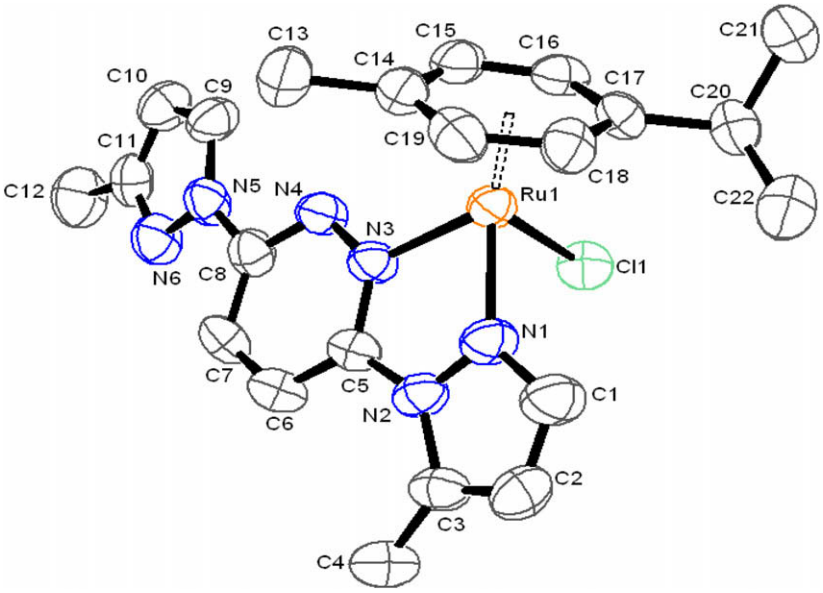

Fig. 8. Molecular structure of complex [(η^6-*p*-cymene)Ru(L3)Cl]ClO_4 [**11**]ClO_4 with 50% probability thermal ellipsoids.

Table 2
Selected bond lengths and angles for ligand **L3** and complexes [**1**]PF_6, [**3**]PF_6, [**10**]PF_6 and [**11**]ClO_4.

Distances (Å)	**L3**	[**1**]PF_6	[**3**]PF_6	[**10**]PF_6	[**11**]ClO_4
N(1)–Ru		2.082(3)	2.084(4)	2.073(2)	2.054(5)
N(3)–Ru		2.071(3)	2.070(3)	2.062(3)	2.075(5)
N(1)–N(2)	1.374(3)	1.365(5)	1.380(5)	1.391(3)	1.358(7)
N(3)–N(4)	1.347(4)	1.335(5)	1.346(5)	1.341(3)	1.346(7)
N(5)–N(6)	1.370(3)			1.377(3)	1.362(7)
Ru–Cl(1)		2.3932(11)	2.4048(12)	2.3974(13)	2.4059(19)
Ru–centroid		1.681	1.689	1.686	1.685
Angles (°)					
N(1)–Ru–N(3)		76.09(14)	75.38(14)	75.50(9)	75.9(2)
Ru–N(1)–N(2)		114.0(3)	115.1(3)	115.15(16)	115.9(4)
N(1)–Ru–Cl(1)		84.80(10)	83.62(11)	86.74(6)	84.32(17)
N(3)–Ru–Cl(1)		83.62(10)	88.62(10)	85.41(7)	84.89(16)

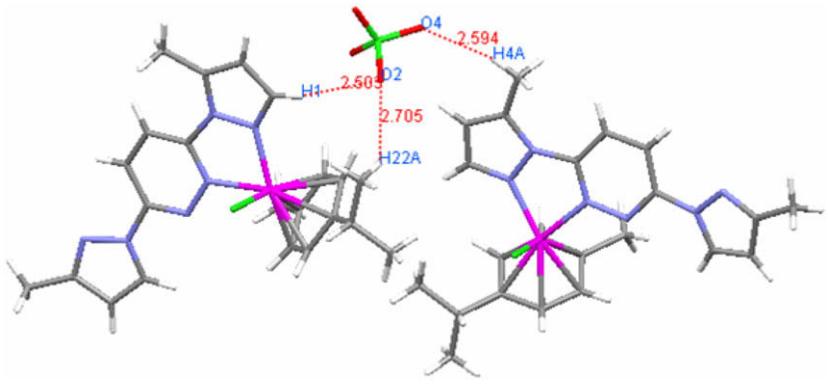

Fig. 9. Diagram showing hydrogen bonding between two adjacent molecular units in [**11**]ClO_4.

3. Conclusion

In summary, a series of η^6-arene ruthenium pyrazolyl-pyridazine complexes which are remarkably stable in the solid state and in solution have been successfully synthesized in good yield. The titled complexes represent a new structural moiety related to the existence of two tautomers in the same compound which are not easily separable by TLC or column chromatography but are easily confirmed by ^{13}C NMR and single crystal X-ray diffraction studies.

4. Experimental

All solvents were dried and distilled prior to use. Ruthenium trichloride trihydrate (Arora Matthey Ltd.), pyrazole; 3-methylpyrazole; 3,5-dimethylpyrazole and 3,6-dichloropyridazine (Aldrich) were purchased and used as received. The ligands were prepared by following a literature procedure [16]. The precursor complexes [(η^6-arene)Ru (μ-Cl)Cl]$_2$ (arene = benzene and *p*-cymene) were prepared by following the literature methods [42–44]. NMR spectra were recorded on an AMX 400 MHz. spectrometer. Infrared spectra were recorded as KBr pellets on a Perkin–Elmer 983 spectrophotometer. Elemental analyses of the complexes were performed on a Perkin–Elmer 2400 CHN/S analyzer. Mass spectra were obtained from a ZQ mass spectrometer by the ESI method. Absorption spectra were obtained at room temperature using a Perkin–Elmer Lambda 25 UV–vis spectrophotometer. All the new complexes gave satisfactory CHN results.

4.1. Single-crystal X-ray structures analyses

Crystals suitable for X-ray diffraction study for complexes [**1**]PF_6, [**3**]PF_6, [**10**]PF_6 and [**11**]ClO_4 were grown by slow diffusion of diethylether into dichloromethane solution of the respective complexes. For the ligand **L3**, crystals were grown by slow evaporation of a chloroform solution of **L3**. The intensity data of the white crystal of **L3**, the bright orange crystal of compound [**1**]PF_6, the red color crystal of [**10**]PF_6 and the yellow crystals of compound [**3**]PF_6 and [**11**]ClO_4 were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube Mo Kα radiation (α = 0.71073 Å) at 273(3) K, with increasing ω (width of 0.3° per frame) at a scan speed of 3 s/frame. The SMART software was used for data acquisition. Data integration and reduction were undertaken with the SAINT and XPREP softwares. Multi-scan empirical absorption corrections were applied to the data using the program SADABS. Structures were solved by direct methods using SHELXS-97 [45] and refined with full-matrix least squares on F^2 using SHELXL-97 [46]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference Fourier maps and refined. Structural illustrations have been drawn with ORTEP-3 [47] for Windows. The ORTEP presentations of the representative complexes are shown in Figs. 4–8, respectively. The bond lengths and angles and data collection parameters are presented in Tables 2 and 3.

4.2. Preparation of cationic complexes [**1**]PF_6 to [**6**]PF_6

4.2.1. Synthesis of [(η^6-*p*-cymene)Ru(Cl–L1)Cl]PF_6 ([**1**]PF_6)

A mixture of [(η^6-*p*-cymene)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.08 mmol), Cl–L1 (28 mg, 0.16 mmol) and 2.5 equivalents of NH_4PF_6 in 15 ml of dry methanol was stirred at room temperature for 4 h producing a color change from light red to deep red. The solvents were removed using a rotary evaporator under reduced pressure, the residue dissolved in dichloromethane (10 ml), and the solution filtered to remove ammonium chloride. The solution was concentrated to 5 ml, when addition of excess diethylether gave the yellow complex, which was separated and dried under vacuum.

Yield: 69 mg, 70.9%.

Elemental Anal. Calc. for $C_{17}H_{19}N_4RuCl_2PF_6$: C, 34.24; H, 3.21; N, 9.40. Found: C, 33.92; H, 3.33; N, 9.49%.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.02 (d, $^3J_{H,H}$ = 9.6 Hz, 2H), 7.85 (d, $^3J_{H,H}$ = 9.6 Hz, 2H), 6.39 (t, $^3J_{H,H}$ = 8.0 Hz, 1H), 5.90 (d, $^3J_{H,H}$ = 6.4 Hz, 1H, $Ar_{p\text{-}cy}$), 5.84 (d, $^3J_{H,H}$ = 6.4 Hz, 1H, $Ar_{p\text{-}cy}$), 5.76 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $Ar_{p\text{-}cy}$), 5.69 (d, $^3J_{H,H}$ = 6.0 Hz,1H, $Ar_{p\text{-}cy}$), 2.99 (sep, $^3J_{H,H}$ = 6.8 Hz, 1H), 2.19 (s, 3H), 1.32 (d, $^3J_{H,H}$ = 7.2 Hz, 3H), 1.29 (d, $^3J_{H,H}$ = 6.8 Hz, 3H). ESI-MS (*m*/*z*): 451.2 [M−PF_6], 415.1 [M−PF_6−Cl].

4.2.2. Synthesis of [(η^6-C_6H_6)Ru(Cl–L1)Cl]PF_6 ([**2**]PF_6)

A mixture of [(η^6-C_6H_6)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.10 mmol), Cl–L1 (36 mg, 0.020 mmol) and 2.5 equivalents of NH_4PF_6 in 15 ml of dry methanol was stirred at room temperature for 4 h. The brown compound which formed was filtered, washed with methanol and diethylether and dried under vacuum.

Yield: 65 mg, 60.2%.

Elemental Anal. Calc. for $C_{13}H_{11}N_4RuCl_2PF_6$: C, 28.90; H, 2.05; N, 10.37. Found: C, 29.05; H, 1.98; N, 10.55%.

^{1}H NMR (400 MHz, CD_3CN, 25 °C, TMS): δ = 8.20 (d, $^3J_{H,H}$ = 9.6 Hz, 2H), 7.91 (d, $^3J_{H,H}$ = 9.6 Hz, 2H), 6.44 (t, $^3J_{H,H}$ = 8.0 Hz, 1H), 6.12 (s, 6H, C_6H_6). ESI-MS (*m*/*z*): 395.1 [M−PF_6].

4.2.3. Synthesis of [(η^6-*p*-cymene)Ru(Cl–L2)Cl]PF_6 ([**3**]PF_6)

A mixture of [(η^6-*p*-cymene)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.08 mmol), Cl-L2 (34 mg, 0.16 mmol) and 2.5 equivalents of NH_4PF_6 in 15 ml of dry methanol was stirred at room temperature for 4 h producing a red to yellow color change. The solvents were reduced using a rotary evaporator under reduced pressure, the residue dissolved in dichloromethane (10 ml), and the solution filtered to remove ammonium chloride. The solution was concentrated to 5 ml, when addition of excess diethylether gave the yellow complex, which was separated and dried under vacuum.

Yield: 65 mg, 63.9%.

Elemental Anal. Calc. for $C_{19}H_{23}N_4RuCl_2PF_6$: C, 36.55; H, 3.71; N, 8.97. Found: C, 36.43; H, 3.79; N, 9.01%.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.05 (d, $^3J_{H,H}$ = 9.6 Hz, 1H), 7.85 (d, $^3J_{H,H}$ = 9.6 Hz, 1H), 6.40 (s, 1H), 5.96 (d, $^3J_{H,H}$ = 6.4 Hz, 1H, $Ar_{p\text{-}cy}$), 5.85 (d, $^3J_{H,H}$ = 6.4 Hz, 1H, $Ar_{p\text{-}cy}$), 5.80 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $Ar_{p\text{-}cy}$), 5.75 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $Ar_{p\text{-}cy}$), 2.91 (sep, $^3J_{H,H}$ = 6.8 Hz, 1H), 2.20 (s, 6H, CH_3), 2.1 (s, 3H), 1.35 (d, $^3J_{H,H}$ = 7.2 Hz, 3H), 1.29 (d, $^3J_{H,H}$ = 6.8 Hz, 3H). ESI-MS (*m*/*z*): 479.2 [M−PF_6].

4.2.4. Synthesis of [(η^6-C_6H_6)Ru(Cl–L2)Cl]PF_6 ([**4**]PF_6)

A mixture of [(η^6-C_6H_6)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.10 mmol), Cl–L2 (41 mg, 0.20 mmol) and 2.5 equivalents of NH_4PF_6 in 15 ml of dry methanol was stirred at room temperature for 4 h. The brown compound which formed was filtered, washed with methanol and diethylether and dried under vacuum.

Yield: 67 mg, 59.0%.

Elemental Anal. Calc. for $C_{15}H_{15}N_4RuCl_2PF_6$: C, 31.70; H, 2.66; N, 9.86. Found: C, 32.37; H, 2.45; N, 9.72%.

^{1}H NMR (400 MHz, DMSO–d_6, 25 °C, TMS): δ = 8.44 (d, $^3J_{H,H}$ = 9.6 Hz, 1H), 8.22 (d, $^3J_{H,H}$ = 9.6 Hz, 1H), 6.53 (s, 1H), 6.04 (s, 6H, C_6H_6), 2.71 (s, 6H, CH_3). ESI-MS (*m*/*z*): 422.7 [M−PF_6].

4.2.5. Synthesis of [(η^6-*p*-cymene)Ru(Cl–L3)Cl]PF_6 ([**5**]PF_6)

A mixture of [(η^6-*p*-cymene)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.08 mmol), Cl–L3 (31 mg, 0.16 mmol) and 2.5 equivalents of NH_4PF_6 in 15 ml of dry methanol was stirred at room temperature for 4 h producing a red to yellow color change. The solvents were removed using a

Table 3
Crystallographic and structure refinement parameters for the ligand (**L3**) and complexes [**1**]PF_6, [**3**]PF_6, [**10**]PF_6 and [**11**]ClO_4.

Compound	**L3**	[**1**]PF_6	[**3**]PF_6	[**10**]PF_6	[**11**]ClO_4
Empirical formula	$C_{12}H_{12}N_6$	$C_{17}H_{19}Cl_2F_6RuN_4P$	$C_{19}H_{23}Cl_2F_6N_4PRu$	$C_{20}H_{22}ClF_6N_6PRu$	$C_{22}H_{26}Cl_2N_6RuO_4$
Formula weight	240.28	596.30	624.35	627.93	610.46
Temperature (K)	296(2)	296(2)	296(2)	170(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$	Monoclinic, $C2/c$	Triclinic, $P\bar{1}$	Monoclinic, $P\,2(1)/c$
Unit cell dimensions					
a (Å)	5.9546(6)	13.7823(2)	15.3266(3)	7.823(4)	14.8458(9)
b (Å)	9.2459(9)	11.0438(2)	12.1360(3)	12.081(7)	16.0246(10)
c (Å)	11.1289(11)	14.7558(2)	25.5224(6)	13.352(7)	11.3289(7)
μ (°)	85.832(7)	96.8950(10)	94.988(2)	72.463(8)	112.201(3)
β (°)	87.678(7)			73.762(8)	
γ (°)	73.043(6)			79.764(9)	
Volume (A^3)	584.40(10)	2229.72(6)	4729.28(19)	1149.2(11)	2496.9(3)
Z, calculated density (Mg/m^3)	2, 1.365	4, 1.776	8, 1.754	2, 1.815	4, 1.624
Absorption coefficient (mm^{-1})	0.090	1.077	1.019	0.940	0.883
$F(0\,0\,0)$	252	1184	2496	628	1240
Crystal size (mm)	0.48 × 0.24 × 0.18	0.48 × 0.16 × 0.12	0.45 × 0.20 × 0.11	0.28 × 0.17 × 0.15	0.35 × 0.20 × 0.15
θ range for data collection (°)	1.84–28.28	1.49–28.29	2.14–28.32	1.78–28.32	1.95–28.37
Index ranges	$-7 \leqslant h \leqslant 7$, $-12 \leqslant k \leqslant 12$, $-14 \leqslant l \leqslant 14$	$-16 \leqslant h \leqslant 18$, $-14 \leqslant k \leqslant 14$, $-19 \leqslant l \leqslant 19$	$-20 \leqslant h \leqslant 20$, $-15 \leqslant k \leqslant 16$, $-33 \leqslant l \leqslant 33$	$-10 \leqslant h \leqslant 10$, $-16 \leqslant k \leqslant 16$, $-17 \leqslant l \leqslant 17$	$-19 \leqslant h \leqslant 19$, $-14 \leqslant k \leqslant 21$, $-15 \leqslant l \leqslant 10$
Reflections collected/ unique [R_{int} = 0.2224]	7613/2722 [R_{int} = 0.0277]	26 791/5432 [R_{int} = 0.0312]	36 312/5813 [R_{int} = 0.0378]	15 829/5711 [R_{int} = 0.0400]	22 034/6211 [R_{int} = 0.0511]
Refinement method (F^2)		Full-matrix least-squares on			
Completeness to θ (°)	28.28, 94.2	28.29, 98.0	28.32, 98.5	25.00, 100.0	28.37, 99.4
Data/restraints/parameters	2722/0/166	5432/0/283	5813/0/303	5711/0/320	6211/0/321
Goodness-of-fit on (F^2)	1.015	1.064	1.046	1.021	1.029
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0731, wR_2 = 0.2040	R_1 = 0.0478, wR_2 = 0.1287	R_1 = 0.0517, wR_2 = 0.1348	R_1 = 0.0384, wR_2 = 0.0940	R_1 = 0.0757, wR_2 = 0.1879
R indices (all data)	R_1 = 0.1003, wR_2 = 0.2146	R_1 = 0.0673, wR_2 = 0.1403	R_1 = 0.0765, wR_2 = 0.1477	R_1 = 0.0459, wR_2 = 0.0986	R_1 = 0.1363, wR_2 = 0.2172
Largest difference in peak and hole (A^{-3})	0.245 and −0.213	0.597 and −0.583	0.725 and −0.677	1.029 and −0.632	0.574 and −0.475

rotary evaporator under reduced pressure, the residue dissolved in dichloromethane (10 ml), and the solution filtered to remove ammonium chloride. The solution was concentrated to 5 ml, when addition of excess diethylether gave the yellow complex, which was separated and dried under vacuum.

Yield: 66 mg, 66.3%.

Elemental Anal. Calc. for $C_{18}H_{21}N_4RuCl_2PF_6$: C, 35.42; H, 3.47; N, 9.18. Found: C, 35.61; H, 3.11; N, 9.34%.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.58 (d, $^3J_{H,H}$ = 5.6 Hz, 1H), 8.32 (d, $^3J_{H,H}$ = 6.4 Hz, 1H), 8.21 (d, $^3J_{H,H}$ = 5.6 Hz, 1H), 7.92 (d, $^3J_{H,H}$ = 6.0 Hz, 1H), 6.12 (d, $^3J_{H,H}$ = 6.4 Hz, 1H, $Ar_{p\text{-}cy}$), 5.98 (d, $^3J_{H,H}$ = 6.4 Hz, 1H, $Ar_{p\text{-}cy}$), 5.86 (d, $^3J_{H,H}$ = 5.6 Hz, 1H, $Ar_{p\text{-}cy}$), 5.79 (d, $^3J_{H,H}$ = 5.6 Hz, 1H, $Ar_{p\text{-}cy}$), 3.22 (sep, $^3J_{H,H}$ = 6.8 Hz, 1H), 2.41 (s, 3H, CH_3), 2.31 (s, 3H), 1.53 (d, $^3J_{H,H}$ = 7.2 Hz, 3H), 1.49 (d, $^3J_{H,H}$ = 5.6 Hz, 3H). ESI-MS (m/z): 465.2 [M−PF_6], 430.1 [M−PF_6−Cl].

4.2.6. Synthesis of [(η^6-C_6H_6)Ru(Cl–L3)Cl]PF_6 ([**6**]PF_6)

A mixture of [(η^6-C_6H_6)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.10 mmol), Cl–L3 (39 mg, 0.20 mmol) and 2.5 equivalents of NH_4PF_6 in 15 ml of dry methanol was stirred at room temperature for 4 h. The brown compound which formed was filtered, washed with methanol and diethylether and dried under vacuum.

Yield: 70 mg, 63.3%.

Elemental Anal. Calc. for $C_{14}H_{13}N_4RuCl_2PF_6$: C, 30.34; H, 2.36; N, 10.11. Found: C, 29.97; H, 2.55; N, 10.32%.

^{1}H NMR (400 MHz, CD_3CN, 25 °C, TMS): δ = 8.52 (d, $^3J_{H,H}$ = 2.0 Hz, 1H), 8.39 (d, $^3J_{H,H}$ = 3.6 Hz, 1H), 8.19 (d, $^3J_{H,H}$ = 4.8 Hz, 1H), 7.98 (d, $^3J_{H,H}$ = 7.2 Hz, 1H), 6.25 (s, 6H, C_6H_6), 2.65 (s, 3H, CH_3). ESI-MS (m/z): 408.9 [M−PF_6].

4.3. Preparation of the cationic complexes [**7**]PF_6 to [**10**]PF_6, [**11**]ClO_4 and [**12**]PF_6

4.3.1. Synthesis of [(η^6-*p*-cymene)Ru(L1)Cl]PF_6 ([**7**]PF_6)

A mixture of [(η^6-*p*-cymene)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.08 mmol), L1 (35 mg, 0.16 mmol) and 2.5 equivalents of NH_4PF_6 in 15 ml of dry methanol was stirred at room temperature for 4 h producing a light red to deep red color change. The solvents were removed using a rotary evaporator under reduced pressure, the residue dissolved in dichloromethane (10 ml), and the solution filtered to remove ammonium chloride. The solution was concentrated to 5 ml, when addition of excess diethylether gave the yellow complex, which was separated and dried under vacuum.

Yield: 65 mg, 63.4%.

Elemental Anal. Calc. for $C_{20}H_{22}N_6RuClPF_6$: C, 38.26; H, 3.53; N, 13.38. Found: C, 37.92; H, 3.77; N, 12.95%.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.61 (d, $^3J_{H,H}$ = 2.4 Hz, 1H), 8.59 (d, $^3J_{H,H}$ = 2.4 Hz, 1H), 8.55 (d, $^3J_{H,H}$ = 7.6 Hz, 1H), 8.23 (d, $^3J_{H,H}$ = 6.4 Hz, 1H), 7.90 (d, $^3J_{H,H}$ = 6.4 Hz, 1H), 7.72 (d, $^3J_{H,H}$ = 8.0 Hz, 1H), 6.87 (t, $^3J_{H,H}$ = 6.0 Hz, 1H), 6.48 (t, $^3J_{H,H}$ = 5.6 Hz, 1H), 6.20 (d, $^3J_{H,H}$ = 6.4 Hz, 1H, $Ar_{p\text{-}cy}$), 6.07 (d, $^3J_{H,H}$ = 6.4 Hz, 1H, $Ar_{p\text{-}cy}$), 5.91 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $Ar_{p\text{-}cy}$), 5.82 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $Ar_{p\text{-}cy}$), 2.72 (sep, $^3J_{H,H}$ = 6.2 Hz, 1H), 2.20 (s, 3H), 1.22 (d, $^3J_{H,H}$ = 7.2 Hz, 3H), 1.18 (d, $^3J_{H,H}$ = 7.6 Hz, 3H). ESI-MS (m/z): 483.1 [M−PF_6].

*4.3.2. Synthesis of [(η^6-C_6H_6)Ru(L1)Cl]PF_6 ([**8**]PF_6)*

A mixture of [(η^6-C_6H_6)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.10 mmol), L1 (42 mg, 0.20 mmol) and 2.5 equivalents of NH_4PF_6 in 15 ml of dry methanol was stirred at room temperature for 4 h. The brown compound which formed was filtered, washed with methanol and diethylether and dried under vacuum.

Yield: 66 mg, 57.8%.

Elemental Anal. Calc. for $C_{16}H_{14}N_6RuClPF_6$: C, 33.61; H, 2.47; N, 14.70. Found: C, 33.73; H, 2.65; N, 13.98%.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.72 (d, $^3J_{H,H}$ = 2.4 Hz, 1H), 8.63 (d, $^3J_{H,H}$ = 2.4 Hz, 1H), 8.54 (d, $^3J_{H,H}$ = 7.6 Hz, 1H), 8.44 (d, $^3J_{H,H}$ = 7.6 Hz, 1H), 8.02 (d, $^3J_{H,H}$ = 6.4 Hz, 1H), 7.91 (d, $^3J_{H,H}$ = 6.0 Hz, 1H), 6.92 (t, $^3J_{H,H}$ = 8.0 Hz, 1H), 6.53 (t, $^3J_{H,H}$ = 6.4 Hz, 1H), 5.90 (s, 6H, C_6H_6). ESI-MS (*m*/*z*): 427.2 [M−PF_6].

*4.3.3. Synthesis of [(η^6-*p*-cymene)Ru(L2)Cl]PF_6 ([**9**]PF_6)*

A mixture of [(η^6-*p*-cymene)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.08 mmol), L2 (43 mg, 0.16 mmol) and 2.5 equivalents of NH_4PF_6 in 15 ml of dry methanol was stirred at room temperature for 4 h producing a red to yellow color change. The solvent was reduced using a rotary evaporator under reduced pressure, the residue was dissolved in dichloromethane (10 ml), and the solution filtered to remove ammonium chloride. The solution was concentrated to 5 ml, when addition of excess diethylether gave the yellow complex, which was separated and dried under vacuum.

Yield: 67 mg, 65.6%.

Elemental Anal. Calc. for $C_{24}H_{30}N_6RuClPF_6$: C, 46.06; H, 4.83; N, 13.43. Found: C, 46.73; H, 4.25; N, 13.07%.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.36 (d, $^3J_{H,H}$ = 9.6 Hz, 1H), 8.11 (d, $^3J_{H,H}$ = 9.2 Hz, 1H), 6.54 (s, 2H), 6.05 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $Ar_{p\text{-}cy}$), 5.92 (d, $^3J_{H,H}$ = 6.4 Hz, 1H, $Ar_{p\text{-}cy}$), 5.84 (d, $^3J_{H,H}$ = 6.4 Hz, 1H, $Ar_{p\text{-}cy}$), 5.77 (d, $^3J_{H,H}$ = 6.4 Hz, H, $Ar_{p\text{-}cy}$), 2.71 (s, 12H, CH_3), 2.69 (sep, $^3J_{H,H}$ = 6.0 Hz, 1H), 2.18 (s, 3H), 1.09 (d, $^3J_{H,H}$ = 7.2 Hz, 3H), 1.06 (d, $^3J_{H,H}$ = 6.8 Hz, H). ESI-MS (*m*/*z*): 538.8 [M−PF_6].

*4.3.4. Synthesis of [(η^6-C_6H_6)Ru(L2)Cl]PF_6 ([**10**]PF_6)*

A mixture of [(η^6-C_6H_6)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.10 mmol), L2 (53 mg, 0.20 mmol) and 2.5 equivalents of NH_4PF_6 in 15 ml of dry methanol was stirred at room temperature for 4 h. The brown compound which formed was filtered, washed with methanol and diethylether and dried under vacuum.

Yield: 64 mg, 56.3%.

Elemental Anal. Calc. for $C_{20}H_{22}N_6RuClPF_6$: C, 42.16; H, 3.89; N, 14.75. Found: C, 41.90; H, 4.05; N, 14.33%.

^{1}H NMR (400 MHz, DMSO–d_6, 25 °C, TMS): δ = 8.50 (d, $^3J_{H,H}$ = 9.6 Hz, H), 8.48 (d, $^3J_{H,H}$ = 9.6 Hz, 1H), 7.76 (s, 2H), 5.87 (s, 6H, C_6H_6), 2.78 (s, 12H, CH_3). ESI-MS (*m*/*z*): 483.3 [M−PF_6].

*4.3.5. Synthesis of [(η^6-*p*-cymene)Ru(L3)Cl]ClO_4 ([**11**]ClO_4)*

A mixture of [(η^6-*p*-cymene)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.08 mmol), L3 (39 mg, 0.16 mmol) and 2.5 equivalents of $NaClO_4$ in 15 ml of dry methanol was stirred at room temperature for 4 h producing a red to yellow color change. The solvents were removed using a rotary evaporator under reduced pressure, the residue dissolved in dichloromethane (10 ml), and the solution filtered to remove ammonium chloride. The solution was concentrated to 5 ml, when addition of excess diethylether gave the yellow complex, which was separated and dried under vacuum.

Yield: 73 mg, 73.4%.

Elemental Anal. Calc. for $C_{22}H_{26}N_6RuCl_2O_4$: C, 43.28; H, 4.29; N, 13.77. Found: C, 43.78; H, 3.94; N, 13.92%.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.53 (d, $^3J_{H,H}$ = 10.0 Hz, 1H), 8.45 (d, $^3J_{H,H}$ = 2.4 Hz, 1H), 8.27 (s, 1H), 8.19 (d, $^3J_{H,H}$ = 9.6 Hz, H), 6.44 (d, $^3J_{H,H}$ = 2.4 Hz, 1H), 6.34 (d, $^3J_{H,H}$ = 2.4 Hz, 1H), 5.93 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $Ar_{p\text{-}cy}$), 5.87 (d, $^3J_{H,H}$ = 6.4 Hz, 1H, $Ar_{p\text{-}cy}$), 5.76 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $Ar_{p\text{-}cy}$), 5.68 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $Ar_{p\text{-}cy}$), 3.1 (sep, $^3J_{H,H}$ = 6.8 Hz, 1H), 2.39 (s, 6H, CH_3), 2.26 (s, 3H), 1.42 (d, $^3J_{H,H}$ = 7.2 Hz, 3H), 1.38 (d, $^3J_{H,H}$ = 7.2 Hz, 3H).ESI-MS (*m*/*z*): 511.3 [M−ClO_4].

*4.3.6. Synthesis of [(η^6-C_6H_6)Ru(L3)Cl]PF_6 ([**12**]PF_6)*

A mixture of [(η^6-C_6H_6)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.10 mmol), L3 (48 mg, 0.20 mmol) and 2.5 equivalents of NH_4PF_6 in 15 ml of dry methanol was stirred at room temperature for 4 h. The brown compound which formed was filtered, washed with methanol and diethylether and dried under vacuum.

Yield: 56 mg, 51.78%.

Elemental Anal. Calc. for $C_{18}H_{18}N_6RuClPF_6$: C, 39.91; H, 3.35; N, 15.51. Found: C, 40.22; H, 3.08; N, 14.92%.

^{1}H NMR (400 MHz, CD_3CN, 25 °C, TMS): δ = 8.53 (d, $^3J_{H,H}$ = 9.6 Hz, 1H), 8.46 (d, $^3J_{H,H}$ = 10.4 Hz, H), 8.42 (s, 1H), 8.31 (d, $^3J_{H,H}$ = 9.6 Hz, 1H), 8.21 (d, $^3J_{H,H}$ = 9.6 Hz, H), 6.76 (d, $^3J_{H,H}$ = 2.8 Hz, 1H), 6.09 (s, 6H, C_6H_6), 2.76 (s, 6H,CH_3). ESI-MS (*m*/*z*): 455.2 [M−PF_6], 419.2 [M−PF_6−Cl].

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Appendix A. Supplementary material

CCDC 710387 (**L3**), 710388 ([**1**]PF6), 710389 ([**3**]PF6), 710390 ([**10**]PF6) and 710391 ([**11**]ClO4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.03.043.

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