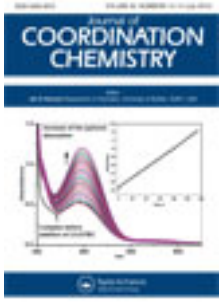

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Syntheses and structural studies of mononuclear arene ruthenium complexes with nitrogen-based chelating ligands

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Syntheses and structural studies of mononuclear arene ruthenium complexes with nitrogen-based chelating ligands

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Dinuclear arene ruthenium complexes $[(\eta^6\text{-arene})Ru(\mu\text{-Cl})Cl]_2$ (arene = C_6H_6; $p^iPrC_6H_4Me$; C_6Me_6) and monomeric cyclopentadienyl complexes $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$ (Cp = cyclopentadienyl) react with polypyridyl nitrogen ligands L^1 (3-(pyridin-2-yl)-1H-1,2,4-triazole) and L^2 (1,3-bis(di-2-pyridylaminomethyl)benzene) in methanol to afford cationic mononuclear compounds $[(\eta^6\text{-arene})Ru(L^1)Cl]^+$ (arene = C_6H_6, **1**; $p^iPrC_6H_4Me$, **2**; C_6Me_6, **3**), $[(\eta^6\text{arene})Ru(L^2)Cl]^+$ (arene = C_6H_6, **4**; $p^iPrC_6H_4Me$, **5**; C_6Me_6, **6**), $[(\eta^5\text{-Cp})Ru(L^1)(PPh_3)]^+$ (**7**), and $[(\eta^5Cp)Ru(L^2)(PPh_3)]^+$ (**8**). All cationic mononuclear compounds were isolated as their hexafluorophosphate salts and characterized by elemental analyses, NMR, and IR spectroscopic methods and some representative complexes by UV-Vis spectroscopy. The solid state structures of two derivatives, [**6**]PF_6 and [**7**]PF_6, have been determined by the X-ray structure analysis.

Keywords: Arene ruthenium compounds; Nitrogen-based chelating ligands; Crystal structures

1. Introduction

Mononuclear compounds of platinum group metals containing nitrogen-based ligands have received attention for their photochemical properties [1–5], catalytic activities [6–12], electrochemical behavior [13–16], and in the development of new biologically active agents [17–21]. In particular, η^6-arene metal complexes have emerged as versatile intermediates in the organic synthesis as a consequence of the availability of three labile coordinate sites and rigid arene ring occupying another three coordinate sites [22, 23]. Half-sandwich complexes have potential applications as catalyst precursors for hydrogen transfer [24, 25], ring opening metathesis polymerization [26, 27], and olefin oxidation [28]. Arene ruthenium compounds have also been extensively investigated for promising antibacterial and anticancer activities [29, 30]. The arene

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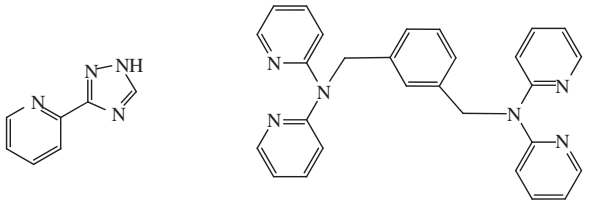


L^1 L^2

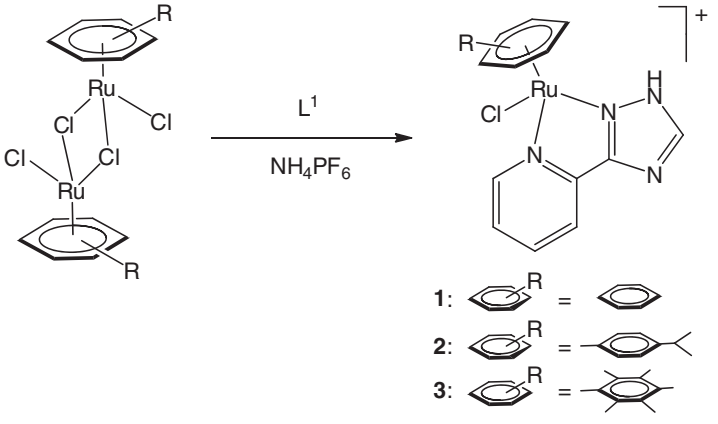
Figure 1. The nitrogen-based chelating ligands 3-(pyridin-2-yl)-1H-1,2,4-triazole (L^1) and 1,3-bis(di-2-pyridylaminomethyl)benzene (L^2).

confers stability to ruthenium in its +2 oxidation state and the characteristic "piano stool" structure offers the possibility to vary the ligands *via* substitution of halide(s) with a variety of σ-donors ranging from tertiary phosphines [31] to β-diketones [32] to aliphatic as well as aromatic amines [33–35]. We have been carrying out reactions of η^5- and η^6-arene metal complexes with a variety of nitrogen-based ligands [36–43], including various polypyridyl ligands. Ruthenium compounds of these types of nitrogen-based ligands function as catalysts for the oxidation of water to dioxygen [44, 45]. Herein we describe the syntheses of eight stable, mononuclear arene ruthenium compounds with nitrogen-based chelating ligands L^1 (3-(pyridin-2-yl)-1H-1,2,4-triazole) and L^2 (1,3-bis(di-2-pyridylaminomethyl)benzene) (figure 1). All compounds are fully characterized by elemental analyses, IR and NMR spectroscopic methods, and some compounds by UV-Vis spectroscopy. To confirm the molecular structures of the mononuclear cations, two compounds have been characterized by single-crystal X-ray diffraction study.

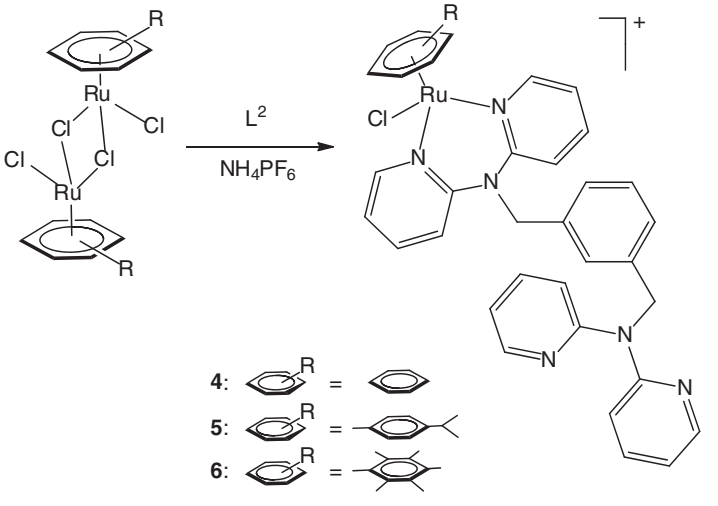
2. Results and discussion

The reactions of dinuclear arene ruthenium complexes $[(\eta^6\text{-arene})Ru(\mu\text{-Cl})Cl]_2$ with two equivalents of L^1 and L^2 in methanol result in cationic mononuclear compounds $[(\eta^6\text{-}C_6H_6)Ru(L^1)Cl]^+$ (**1**), $[(\eta^6\text{-}p^iPrC_6H_4Me)Ru(L^1)Cl]^+$ (**2**), $[(\eta^6C_6Me_6)Ru(L^1)Cl]^+$ (**3**), $[(\eta^6\text{-}C_6H_6)Ru(L^2)Cl]^+$ (**4**), $[(\eta^6\text{-}p^iPrC_6H_4Me)Ru(L^2)Cl]^+$ (**5**), and $[(\eta^6C_6Me_6)Ru(L^2)Cl]^+$ (**6**), isolated as their hexafluorophosphate salts (schemes 1 and 2). Compounds [**1**] PF_6 and [**4**]PF_6 are brown while the others are yellow. These salts are non-hygroscopic and stable in air as well as in the solution. They are sparingly soluble in polar solvents like dichloromethane, chloroform, acetone, and acetonitrile, and insoluble in non-polar solvents. The analytical data of these compounds are consistent with the formulations.

IR spectra exhibit sharp bands due to the bis-chelating L^1 and L^2 at 3439–3436, 1629–1623, and 1471–1455 cm^{-1} corresponding, respectively, to ν_{N-H}, $\nu_{C=C}$, and $\nu_{C=N}$ of these compounds (Section 3). All infrared spectra contain a strong band between 842 and 846 cm^{-1} due to ν_{P-F} of PF_6^-. ^1H NMR spectra of these compounds were recorded in $CDCl_3$ and spectroscopic data are summarized in Section 3. A downfield shift in the position of ^1H NMR spectra of these metal complexes is observed as compared to uncoordinated ligands. The uncoordinated ligands display signals between 9.23–7.46 for L^1 and 7.79–5.11 ppm for L^2, whereas in metal compounds these signals are shifted to 9.50–7.52 ppm for compounds with L^1 and 8.38–5.31 ppm for complexes with L^2.



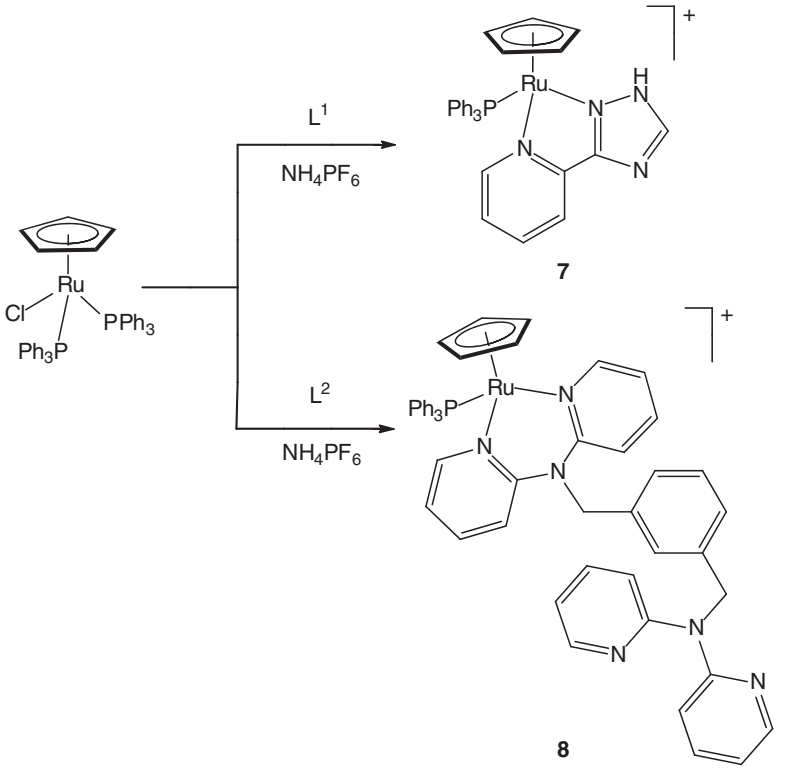
Scheme 1. Synthesis of the monocationic compounds [**1**]PF_6–[**3**]PF_6.



Scheme 2. Synthesis of the monocationic compounds [**4**]PF_6–[**6**]PF_6.

In addition to the aromatic protons from the ligand skeleton, **1** and **4** show singlets at 6.01 and 5.31 ppm, which correspond to the protons of benzene of these compounds. The NMR spectra of **2** and **5** exhibit two doublets at 6.43–5.01 ppm, which correspond to CH protons of *p*-cymene. These compounds also exhibit singlets at 2.28 and 2.22 ppm, doublets at 0.97 and 0.95 ppm, and septets at 2.72 and 2.37 ppm for protons of methyl and isopropyl of *p*-cymene. Compounds **3** and **6** exhibit sharp singlets at 2.16 and 1.98 ppm for the hexamethylbenzene.

One equivalent of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ reacts with L^1 and L^2 in refluxing methanol to give the corresponding mononuclear compounds **7** and **8**, which are isolated as their hexafluorophosphate salts (scheme 3). The cationic compounds **7** and **8** are soluble in halogenated solvents and polar organic solvents such as tetrahydrofuran, methanol, or dimethylsulfoxide, but insoluble in non-polar solvents. All these compounds are stable in



Scheme 3. Synthesis of [**7**]PF_6 and [**8**]PF_6.

solid state as well as in solution. The analytical data of **7** and **8** are consistent with the formulations. Besides IR bands mentioned in Section 3, these compounds have a strong band between 842 and 846 cm^{-1} due to ν_{P-F}. The ^1H and $^{31}P\{^1H\}$ NMR spectra of compounds in $CDCl_3$ are summarized in Section 3. Shift in the position of signals associated with protons of L^1 and L^2 suggest the coordination of nitrogen to ruthenium. The protons of the ligands in these compounds show downfield shifts with respect to protons of the uncoordinated ligand. The downfield shift of the proton signals might result from change in the electron density on ruthenium due to the chelation of the ligand. In addition to the aromatic protons from the ligand skeleton, the ^1H NMR spectra of these complexes show singlets at 4.57 and 4.68 ppm, which correspond to cyclopentadienyl of these compounds. The protons of triphenylphosphine of **7** and **8** exhibit a large multiplet centered at 7.20 ppm. In $^{31}P\{^1H\}$ NMR spectra of **7** and **8**, the ^{31}P nuclei of the coordinated PPh_3 resonated as a sharp singlet at 50.85 and 50.81 ppm, respectively, whereas in the starting precursor the signal appears upfield. The ^{31}P NMR spectra also show a septet at −143 ppm, which is due to the ^{31}P of PF_6.

2.1. *Molecular structures of 6 and 7*

Compound **6** shows a three-legged piano-stool geometry with Ru(II) being coordinated by hexamethylbenzene, a terminal chloride, and L^2 *N,N*-chelating, as displayed

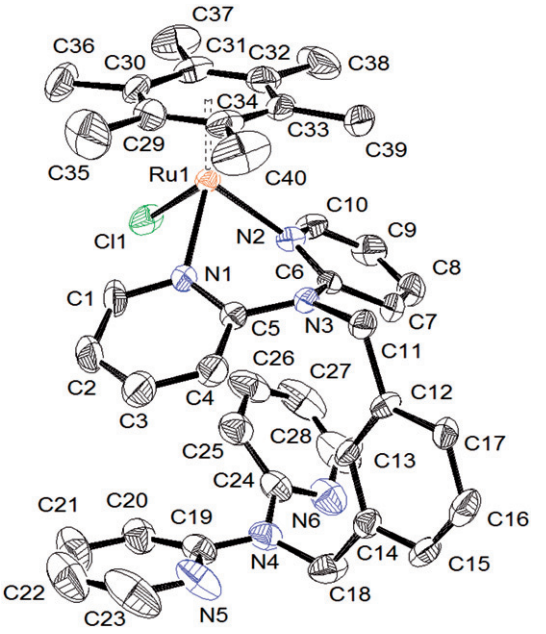


Figure 2. ORTEP diagram of **6**. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms and PF_6^- are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1–Cl1 2.388(1), Ru1–N1 2.084(4), Ru1–N2 2.087(4), N3–C5 1.391(6), N3–C6 1.404(6), N3–C11 1.474(6), N4–C18 1.460(7), N4–C19 1.408(7), N4–C24 1.404(7); N1–Ru1–N2 80.5(1), N1–Ru1–Cl1 86.9(1), N2–Ru1–Cl1 86.8(1), C5–N3–C6 123.0(3), C5–N3–C11 117.9(4), C6–N3–C11 117.1(4), C18–N4–C19 118.9(4), C18–N4–C24 116.6(5), C19–N4–C24 123.9(4).

in figure 2. The 1,3-bis(di-2-pyridylaminomethyl)benzene is bidentate through two adjacent pyridyl groups, and Ru–N distances are equivalent at 2.084(4) and 2.087(4) Å, respectively. The aromatic ring of hexamethylbenzene is planar and the Ru–centroid distance is 1.689 Å. The Ru–Cl distance is 2.383(1) Å, similar to those found in other chloride arene ruthenium compounds [46, 47]. In 1,3-bis(di-2-pyridylaminomethyl)benzene, the tertiary amines are closer to trigonal planar than tetrahedral geometry, the C–N–C angles ranging from 116.6(5)° to 123.9(4)°. The major distortion imposed on the 1,3-bis(di-2-pyridylaminomethyl)benzene structure upon coordination is observed in orientation of the pyridyl groups. On the free side of the ligand, the two pyridyl groups approach a *trans* orientation with respect to each other [48], while on the coordination side, the pair of pyridyl groups coordinated to the Ru are *cis*.

In the crystal packing, the chloride interacts weakly with a C–H of a neighboring cation, thus forming one-dimensional chains along the *a* axis. The H–Cl and C–Cl separations are 2.802 and 3.707 Å with the C–H···Cl angle being 164.36° (figure 3). The presence of hexafluorophosphate gives multiple weak intermolecular C–H···F interactions in the crystal.

In **7**, Ru(II) is octahedrally coordinated to a triphenylphosphine, a cyclopentadienyl and bidentate L^1. The 3-(pyridin-2-yl)-1,2,4-triazole, which shows almost perfect planarity, forms a five-membered metallacycle upon coordination to ruthenium. The aromatic ring of the cyclopentadienyl is planar and the Ru–centroid distance is 1.824 Å. The Ru–P bond length is 2.314(1) Å, while the Ru–N (pyridyl) distance is 2.119(3) Å and the Ru–N (triazole) distance is 2.089(4) Å, as displayed in figure 4. This Ru–P bond

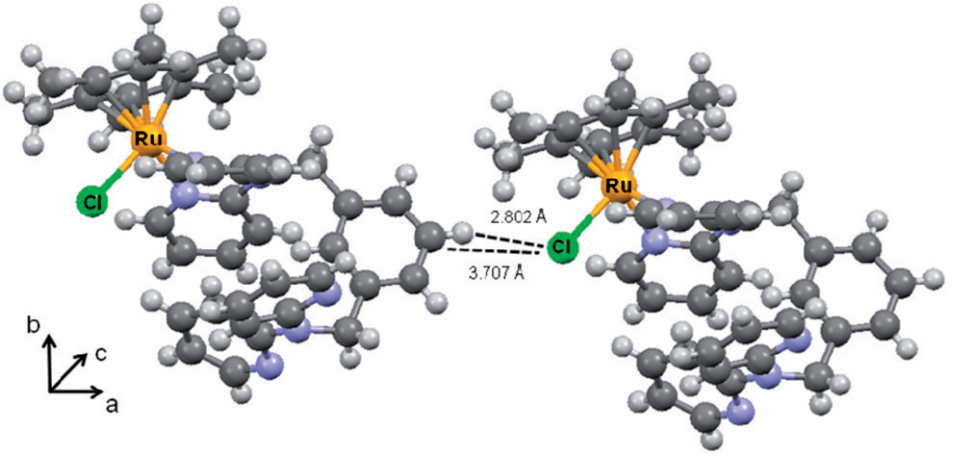


Figure 3. The inter-molecular C–H···Cl contacts in the crystal of [**6**]PF_6.

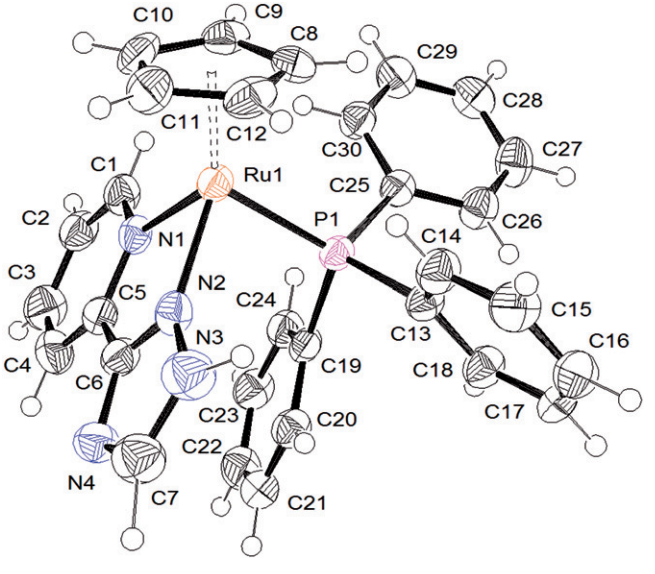


Figure 4. ORTEP diagram of **7**. Displacement ellipsoids are shown at the 50% probability level. PF_6^- is omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1–P1 2.314(1), Ru1–N1 2.119(3), Ru1–N2 2.089(4), N2–N3 1.390(5), N1–C5 1.352(6), N2–C6 1.320(6), C5–C6 1.452(6); N1–Ru1–N2 76.0(1), N1–Ru1–P1 90.2(1), N2–Ru1–P1 87.7(1), N3–N2–C6 105.8(4), N2–C6–C5 119.5(4), C6–C5–N1 111.1(4), C1–N1–C5 117.0(4).

distance is similar to those found [average Ru–P value of 2.32 Å] in other [(arene)Ru(PPh_3)(*N*,*N*)] compounds (*N*,*N* = 3,5-bis(2-pyridyl)pyrazole [36], 2-(2′-pyridyl)benzimidazole [49], and 3-chloro-6-(3,5-dimethylpyrazolyl)pyridazine [50]). Ru–N distances are comparable to those found in the related [(arene)RuCl(*N*,*N*)] compounds, *N*,*N* = 1,3-bis(3-(pyridine-2-yl)-1*H*-pyrazol-1-yl)methyl)benzene [40] and *N*,*N* = 2-(pyridine-2-yl)thiazole [51], in which the Ru–N distances are between 2.07(1)

Table 1. UV-Vis absorption data in acetonitrile at 298 K.

Compound	λ_{max} (nm) ($\varepsilon/10^{-4}$ (mol L^{-1})$^{-1}$ cm^{-1})		
[**2**]PF_6	234 (0.62)	291 (0.80)	396 (0.06)
[**3**]PF_6		289 (0.89)	426 (0.07)
[**4**]PF_6	251 (0.83)	284 (0.71)	416 (0.02)
[**5**]PF_6	233 (1.04), 256 (1.07)	296 (0.80)	394 (0.06)
[**7**]PF_6	274 (0.59)	278 (0.42)	385 (0.06)
[**8**]PF_6		291 (0.28)	399 (0.06)

and 2.15(1) Å. No significant directional interactions between adjacent mononuclear ruthenium compounds or with the hexafluorophosphate are observed in the crystal packing. However, an intramolecular slipped-parallel π-stacking interaction is observed between the pyridyl ring of L^1 and one phenyl ring (C19–C24) of triphenylphosphine: the centroid···centroid separation is 3.63 Å.

2.2. *UV-Vis spectroscopy*

UV-Vis spectra of **2**–**5**, **7**, and **8** (Supplementary material) were acquired in acetonitrile and the spectral data are summarized in table 1. The Ru(II) possesses a low-spin d^6 configuration, and consequently the filled orbitals can interact with low-lying π^* orbitals of the ligands. Therefore, one should expect metal-to-ligand charge transfer (MLCT) transition in their electronic spectra [52, 53]. Indeed, medium intensity bands are observed in the UV-Vis region. The lowest energy absorptions in the electronic spectra of these compounds in the visible region ~426–385 nm have been tentatively assigned on the basis of their intensity and position to MLCT transitions, while bands on the high energy side of the spectra are assigned to ligand-centered $\pi\rightarrow\pi^*/n\rightarrow\pi^*$ transitions [54, 55]. In general, these compounds follow the normal trends observed in electronic spectra of nitrogen-bonded metal compounds, which display a ligand-based $\pi\rightarrow\pi^*$ transition for nitrogen-based ligands in the UV region and MLCT transitions in the visible region.

3. Experimental

3.1. *Physical measurements*

Infrared spectra were recorded on a Perkin-Elmer Model 983 spectrophotometer with the sample prepared as KBr pellets. NMR spectra were obtained using a Bruker Avance II 400 spectrometer in $CDCl_3$ for complexes using TMS as an internal standard. All chemicals used were of reagent grade. Elemental analyses of the complexes were performed on a Perkin-Elmer 2400 CHN/S analyzer. Absorption spectra were obtained at room temperature using a Perkin-Elmer Lambda 25 UV-Vis spectrophotometer. All reactions were carried out in distilled and dried solvents. L^1 and L^2 were prepared by following a reported procedure [56, 57]. The precursor complexes [(η^6-arene)Ru(μ-Cl)Cl]$_2$ (arene = C_6H_6, p^iPrC_6H_4Me and C_6Me_6) and [(η^5-C_5H_5)Ru(PPh_3)$_2$Cl] were prepared by following the literature methods [58–63].

Table 2. Crystallographic and structure refinement parameters for [**6**]PF_6 and [**7**]PF_6.

	[**6**]PF_6	[**7**]PF_6
Chemical formula	$C_{40}H_{42}ClF_6N_6PRu$	$C_{30}H_{26}F_6N_4P_2Ru$
Formula weight	888.29	719.56
Crystal system	Monoclinic	Monoclinic
Space group	*C c* (no. 9)	*P* $2_1/n$ (no. 14)
Crystal color and shape	Orange plate	Orange block
Crystal size (mm^3)	$0.24 \times 0.10 \times 0.04$	$0.15 \times 0.14 \times 0.08$
Unit cell dimensions (Å, °)		
a	23.0623(9)	13.584(1)
b	11.8841(4)	14.6107(9)
c	17.3464(7)	14.776(2)
β	128.302(1)	101.41(1)
Volume ($Å^3$), *Z*	3730.9(2), 4	2874.6(4), 4
Temperature (K)	173(2)	203(2)
Calculated density ($g{\cdot}cm^{-3}$)	1.581	1.663
Absorption coefficient (mm^{-1})	0.605	0.725
θ range for data collection (°)	2.05–23.70	2.07–26.05
Reflections collected	5200	5605
Independent reflection	4854 [R(int) = 0.0321]	3364 [R(int) = 0.1047]
Goodness-of-fit on F^2	1.028	0.859
Flack parameter	0.00(3)	
Final R indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0338$, $wR_2 = 0.0760$	$R_1 = 0.0458$, $wR_2 = 0.0980$
R indices (all data)	$R_1 = 0.0382$, $wR_2 = 0.0782$	$R_1 = 0.0830$, $wR_2 = 0.1085$
Largest difference peak and hole (e $Å^{-3}$)	0.540 and −0.494	0.690 and −1.199

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

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

Crystal of [**6**]PF_6 and [**7**]PF_6 were mounted either on a Bruker Smart CCD platform or a Stoe Image Plate Diffraction System equipped with a φ circle goniometer using Mo-Kα graphite monochromated radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS–97 [64]. Refinement and all further calculations were carried out using SHELXL–97 [64]. In [**6**]PF_6, hydrogen atoms were included in calculated positions and treated as riding using the SHELXL default parameters, while in [**7**]PF_6 some hydrogen atoms were also found and refined, those of C7 and N3 of the triazole ring. In addition, coordination of the triazole ring to ruthenium was disordered over two positions in 55:45 ratio. The major isomer is presented in figure 4 and the minor isomer is coordinated to ruthenium via N4 of the triazole ring. The non-H atoms were refined anisotropically using weighted full-matrix least-square on F^2. Crystallographic details are summarized in table 2. Figures 2 and 4 were drawn with ORTEP-32 [65].

3.3. *Syntheses*

3.3.1. Preparation of [1]PF_6–[3]PF_6. A mixture of $[(\eta^6\text{-arene})Ru(\mu\text{-Cl})Cl]_2$ (0.17 mmol), L^1 (50 mg, 0.34 mmol), and excess of NH_4PF_6 was stirred in dry methanol (30 mL) for 4 h at room temperature. The yellow compound which formed was filtered, washed with ethanol, diethyl ether, and dried under vacuum.

Compound [**1**]PF_6: Yield: 72 mg, 71%. Anal. Calcd for $C_{13}H_{12}ClN_4PF_6Ru$ (%): C, 30.88; H, 2.40; N, 11.07. Found (%): C, 31.02; H, 2.51; N, 10.99. IR (KBr pellets, cm^{-1}): 3439 (ν_{N-H}); 1624 ($\nu_{C=C}$); 1455 ($\nu_{C=N}$); 846 (ν_{P-F}). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 9.45$ (d, $J = 5.6$ Hz, 1H), 8.31 (t, $J = 7.2$ Hz, 1H), 8.12 (d, $J = 6$ Hz, 1H), 7.82 (t, $J = 7.2$ Hz, 1H), 7.52 (s, 1H), 6.01 (s, 6H, C_6H_6), NH not observed.

Compound [**2**]PF_6: Yield: 65 mg, 71%. Anal. Calcd for $C_{17}H_{20}ClN_4PF_6Ru$ (%): C, 36.35; H, 3.60; N, 9.97. Found (%): C, 36.48; H, 3.71; N, 9.88. IR (KBr pellets, cm^{-1}): 3438 (ν_{N-H}); 1629 ($\nu_{C=C}$); 1459 ($\nu_{C=N}$); 844 (ν_{P-F}). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 9.50$ (d, $J = 6$ Hz, 1H), 8.34 (t, $J = 7.2$ Hz, 1H), 8.17 (d, $J = 7.2$ Hz, 1H), 7.78 (t, $J = 7.2$ Hz, 1H), 7.61 (s, 1H), 6.43 (d, $J = 6$ Hz, 2H, Ar_{p-cy}), 6.01 (d, $J = 6$ Hz, 2H, Ar_{p-cy}), 2.72 (sept., 1H), 2.28 (s, 3H), 0.95 (d, $J = 6.8$ Hz, 6H), NH not observed.

Compound [**3**]PF_6: Yield: 60 mg, 68%. Anal. Calcd for $C_{19}H_{24}ClN_4PF_6Ru$ (%): C, 38.68; H, 4.10; N, 9.50. Found (%): C, 38.61; H, 4.21; N, 9.41. IR (KBr pellets, cm^{-1}): 3436 (ν_{N-H}); 1623 ($\nu_{C=C}$); 1468 ($\nu_{C=N}$); 846 (ν_{P-F}). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 9.41$ (d, $J = 7.2$ Hz, 1H), 8.41 (t, $J = 6.8$ Hz, 1H), 8.12 (d, $J = 7.2$ Hz, 1H), 7.82 (t, $J = 7.2$ Hz, 1H), 7.66 (s, 1H), 2.16 (s, 18H, C_6Me_6), NH not observed.

3.3.2. Preparation of [4]PF_6–[6]PF_6. A mixture of $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (0.056 mmol), L^2 (50 mg, 0.11 mmol), and excess of NH_4PF_6 was stirred in dry methanol (30 mL) for 4 h at room temperature. The yellow compound which formed was filtered, washed with ethanol, diethyl ether, and dried under vacuum.

Compound [**4**]PF_6: Yield: 110 mg, 69%. Anal. Calcd for $C_{34}H_{30}ClN_6PF_6Ru$ (%): C, 50.79; H, 3.76; N, 10.44. Found (%): C, 50.92; H, 3.89; N, 10.38. IR (KBr pellets, cm^{-1}): 1627 ($\nu_{C=C}$); 1461 ($\nu_{C=N}$); 842 (ν_{P-F}). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.34$ (d, $J = 6$ Hz, 2H), 7.81 (d, $J = 6.8$ Hz, 2H), 7.33 (t, $J = 7.2$ Hz, 4H), 7.27 (t, $J = 7.2$ Hz, 5H), 7.09 (d, $J = 7.6$ Hz, 5H), 6.61 (d, $J = 7.2$ Hz, 2H), 6.07 (s, 6H, C_6H_6), 5.31 (s, 4H, CH_2).

Compound [**5**]PF_6: Yield: 96 mg, 68%. Anal. Calcd for $C_{38}H_{38}ClN_6PF_6Ru$ (%): C, 53.07; H, 4.45; N, 9.76. Found (%): C, 53.19; H, 4.57; N, 9.68. IR (KBr pellets, cm^{-1}): 1625 ($\nu_{C=C}$); 1471 ($\nu_{C=N}$); 846 (ν_{P-F}). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.31$ (d, $J = 6.8$ Hz, 2H), 7.90 (d, $J = 6$ Hz, 2H), 7.41 (t, $J = 7.2$ Hz, 4H), 7.30 (t, $J = 7.2$ Hz, 5H), 7.06 (d, $J = 7.2$ Hz, 5H), 6.66 (d, $J = 6$ Hz, 2H), 5.40 (s, 4H, CH_2), 5.22 (d, $J = 7.2$, 2H, Ar_{p-cy}), 5.01 (d, $J = 7.2$, 2H, Ar_{p-cy}), 2.37 (sept., 1H), 2.22 (s, 3H), 0.97 (d, $J = 6.8$ Hz, 6H).

Compound [**6**]PF_6: Yield: 89 mg, 67%. Anal. Calcd for $C_{40}H_{42}ClN_6PF_6Ru$ (%): C, 54.09; H, 4.77; N, 9.45. Found (%): C, 54.15; H, 4.81; N, 9.37. IR (KBr pellets, cm^{-1}): 1629 ($\nu_{C=C}$); 1455 ($\nu_{C=N}$); 844 (ν_{P-F}). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.38$ (d, $J = 6.8$ Hz, 2H), 7.78 (d, $J = 6$ Hz, 2H), 7.49 (t, $J = 7.2$ Hz, 4H), 7.29 (t, $J = 7.2$ Hz, 5H), 7.00 (d, $J = 7.2$ Hz, 5H), 6.63 (d, $J = 6$ Hz, 2H), 5.32 (s, 4H, CH_2), 1.98 (s, 18H, C_6Me_6).

3.3.3. Preparation of [7]PF_6 and [8]PF_6. A mixture of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ (100 mg, 0.14 mmol), L^1 or L^2 (0.14 mmol), and excess of NH_4PF_6 was refluxed in dry methanol (30 mL) for 8 h until the color of the solution changed from pale yellow to orange. The solvent was removed under vacuum, the residue was dissolved in dichloromethane (10 mL), and the solution was filtered to remove ammonium halide. The orange solution was concentrated to 5 mL and upon the addition of diethlyether

the orange-yellow complex precipitated was separated, washed with diethylether, and dried under vacuum.

Compound [**7**]PF_6: Yield: 63 mg, 64%. Anal. Calcd for $C_{30}H_{26}N_4P_2F_6Ru$ (%): C, 50.09; H, 3.64; N, 7.78. Found (%): C, 50.15; H, 3.72; N, 7.71. IR (KBr pellets, cm^{-1}): 3436 (ν_{N-H}); 1631 ($\nu_{C=C}$); 1459 ($\nu_{C=N}$); 842 (ν_{P-F}). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 9.39$ (d, $J = 7$ Hz, 1H), 8.52 (t, $J = 6.8$ Hz, 1H), 8.17 (d, $J = 7.2$ Hz, 1H), 7.88 (t, $J = 7.2$ Hz, 1H), 7.61 (s, 1H), 7.22–7.06 (m, 15H, PPh_3), 4.57 (s, 5H, C_5H_5). ^{31}P $\{^1H\}$ NMR ($CDCl_3$, δ): 50.85 (s, PPh_3), −143 (sept., PF_6), NH not observed.

Compound [**8**]PF_6: Yield: 93 mg, 66%. Anal. Calcd for $C_{51}H_{44}N_6P_2F_6Ru$ (%): C, 60.17; H, 4.36; N, 8.25. Found (%): C, 60.31; H, 4.49; N, 8.12. IR (KBr pellets, cm^{-1}): 1624 ($\nu_{C=C}$); 1460 ($\nu_{C=N}$); 846 (ν_{P-F}). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.44$ (d, $J = 7.2$ Hz, 2H), 7.83 (d, $J = 6.8$ Hz, 2H), 7.55 (t, $J = 7.2$ Hz, 4H), 7.39 (t, $J = 7.2$ Hz, 5H), 7.20–7.12 (m, 15H, PPh_3)7.06 (d, $J = 6.8$ Hz, 5H), 6.63 (d, $J = 6$ Hz, 2H), 5.32 (s, 4H, CH_2), 4.68 (s, 5H, C_5H_5). ^{31}P $\{^1H\}$ NMR ($CDCl_3$, δ): 50.81 (s, PPh_3), −143 (sept., PF_6).

4. Conclusions

A series of stable mononuclear η^5- and η^6-cyclic hydrocarbon ruthenium metal complexes with nitrogen-based chelating ligands 3-(pyridin-2-yl)-1H-1,2,4-triazole (L^1) and 1,3-bis(di-2-pyridylaminomethyl)benzene (L^2) have been synthesized. We get mononuclear Ru complexes by controlling the molar ratio of L^2 with respect to $[(\eta^6\text{-arene})Ru(\mu\text{-Cl})Cl]_2$. The 1 : 2 ratio of $[(\eta^6\text{-arene})Ru(\mu\text{-Cl})Cl]_2$ and L^2 gives mononuclear complexes, whereas 1 : 1 ratio results in dinuclear complexes [66]. The distances of Ru and hexamethylbenzene in **6** are significantly longer than those found in the Ru-benzene complexes [67, 68] having similar structure mainly due to the steric effect. The geometric parameters of **7** are in the range found in the complexes with the similar structure. All the compounds synthesized in this study follow the normal trends observed in electronic spectra of nitrogen-bonded metal compounds. Considering recent demonstrations of biological activities such as cytotoxicity and anticancer activities of half-sandwich Ru complexes, our new complexes having more functional ligation sites can be candidates for further biological studies.

Supplementary material

CCDC 843669 ([**6**]PF_6) and 843670 ([**7**]PF_6) contain the supplementary crystallographic data for this article. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033.

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