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Synthesis, spectral and structural studies of water soluble arene ruthenium (II) complexes containing 2,2'-dipyridyl-N-alkylimine ligand

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Abstract: A series of water soluble complexes of general formula $[(\eta^6\text{-arene})\text{Ru}\{(\text{C}_5\text{H}_4\text{N})_2\text{CNRi}\}\text{Cl}]\text{PF}_6$ have been prepared by the reaction of $[(\eta^6\text{-arene})\text{RuCl}_2]_2$ with appropriate 2,2'-dipyridyl-N-alkylimine ligands (dpNRi) in the presence of NH_4PF_6 (where; R = Me or Et; arene = *p*-cymene, C_6Me_6 , C_6H_6). The 2,2'-dipyridyl-N-alkylimine ligands are prepared by reaction of 2,2'-dipyridyl ketone with the corresponding alkylamine. The complexes are readily obtained as air stable yellow to dark brown solids by simple stirring at room temperature. The complexes are isolated as their hexafluorophosphate salts and characterized on the basis of spectroscopic data. The molecular structure of representative complex $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{(\text{C}_5\text{H}_4\text{N})_2\text{C=N-Me}\}\text{Cl}]\text{PF}_6$ has been determined by single crystal X-ray diffraction studies.

Key words: Arene, ruthenium, dimethylpyridyl ketone, spectroscopy, crystal structure.

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1. Introduction

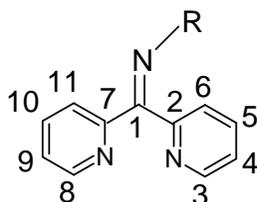
Arene ruthenium (II) complexes play an important role in organometallic chemistry. A lot of interesting chemistry have been generated in the reaction of chlorobridged dimers [$\{(\eta^6\text{-arene})\text{RuCl}_2\}_2$] with various ligands. The chlorobridge dimers [$\{(\eta^6\text{-arene})\text{RuCl}_2\}_2$] are readily cleaved with neutral ligand to give neutral [$(\eta^6\text{-arene})\text{Ru}(\text{L}_1)\text{Cl}_2$] or cationic [$(\eta^6\text{-arene})\text{Ru}(\text{L}_2)\text{Cl}]^+$ complexes (where; L_1 = monodentate and L_2 = bidentate ligand) [1-4]. Recently, water soluble ($\eta^6\text{-arene}$) ruthenium (II) complexes attracted considerable interest owing to their anticancer [5], antitumor [6], antiviral [7] and catalytic properties [8]. Several water soluble $\eta^6\text{-arene}$ ruthenium complexes containing oxygen and nitrogen chelating ligands have been reported in literature [9,10]. It is noteworthy, that among the several ($\eta^6\text{-arene}$) ruthenium (II) complexes reported, nitrogen chelating complexes are the most prominent. Some of these nitrogen chelating $\eta^6\text{-arene}$ ruthenium (II) piano stool complexes studied for potential anticancer activity [11,12].

Furthermore, dipyriddy has been extensively studied in coordination chemistry for the synthesis of transition metal complexes with magnetic properties [13,14]. A large number of mononuclear [15,16] and polynuclear [17,18] coordination compounds have been synthesized using 2,2'-dipyriddy ligands. Dipyriddy can bind as a monodentate or bidentate ligand, thus demonstrating the ability to form mononuclear or dinuclear complexes [19]. As a part of our ongoing study on water soluble $\eta^6\text{-arene}$ ruthenium complexes [9], herein, we described the synthesis and characterization of a series of water soluble ($\eta^6\text{-arene}$) ruthenium (II) complexes containing 2,2'-dipyriddy-N-alkylimine ligands. The molecular structure of the representative complex [$(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{(\text{C}_5\text{H}_4\text{N})_2\text{C}=\text{NMe}\}\text{Cl}\}\text{PF}_6$ (**3[PF₆]**) has been determined by single crystal X-ray diffraction.

2. Experimental

2.1 General remarks: All solvents were dried and distilled prior to use. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was purchased from Arrora Matthey Ltd., India. Methyl amine 2.0 M, Ethyl amine 2.0 M solution and 2,2'-

dipyridylketone were obtained from Sigma Aldrich Pvt. Ltd. Infra red spectra were recorded in a diffused reflection spectroscopy (DRS) assembly with sample prepared in KBr. UV-VIS absorption spectra were obtained on a Shimadzu UV-2401PC spectrometer. NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer at 300.13 (^1H), 75.47 MHz (^{13}C) with SiMe_4 as internal references and coupling constants were given in Hertz. The precursor compound [$\{(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2\}_2$], [$\{(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2\}_2$], [$\{(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2\}_2$] [1,20,21] and the ligand, 2,2'-dipyridyl-*N*-methylimine (dpNmei) was prepared according to published procedure [22] while the ligand 2,2'-dipyridyl-*N*- ethylimine (dpNeti) was prepared following a similar procedure described for dpNmei (scheme 1).



R = Me, dpNmei; Et, dpNeti

Scheme 1

2.2. *Preparation of 2,2'-dipyridyl-N-ethylimine (dpNeti)*: To a solution of 2,2'-dipyridyl ketone (0.100g, 0.540 mmol) in 20 ml of dried methanol was added an ethylamine solution 2.0 M (0.09g, 2mmol). The reaction mixture was heated to reflux for 24 hrs and then allowed to cool. The solvent was removed in a rotary evaporator to give the compound as oily liquid which changed into a light brown solid when refrigerated overnight.

^1H NMR (CDCl_3 , δ): 8.74 (d, 2H, $J = 4.2$), 8.53 (d, 1H, $J = 3.9$), 8.08 (d, 1H, $J = 7.8$), 7.73 (m, 2H), 7.36 (m, 2H), 3.45 (qt, 2H, $J = 7.2$), 1.29 (t, 3H, $J = 7.2$).

2.3 Synthesis of complexes

2.3.1. Synthesis of [$(\eta^6\text{-}p\text{-cymene})\text{Ru}\{(\text{C}_5\text{H}_4\text{N})_2\text{C}=\text{NRi}\}\text{Cl}\}\text{PF}_6$ {R = Me [**1**] PF_6 , Et [**2**] PF_6 }

The complexes were prepared by a general procedure: A mixture of $[(\eta^6\text{-cymene})\text{RuCl}_2]_2$ (0.05g, 0.081 mmol), 2,2'-dipyridyl-N-alkylimine (0.178 mmol) and NH_4PF_6 (0.178 mmol) were stirred in dry MeOH at room temperature for 3 hrs. The colour of the solution turned into dark red as the reaction progressed. The solvent was rotary evaporated and residue was dissolved in minimum amounts of dichloromethane and then filtered. The filtrate on subsequent concentration to *ca.* 3 ml and addition of excess diethyl ether afforded the complexes as a yellow to orange solid.

Yield and spectroscopic data are as follows:

Complex **[1]PF₆**: 0.076g (76%).

FTIR (KBr, cm^{-1}): 1585, 1469, 1438, 842.

^1H NMR (CDCl_3 , δ): 9.47 (d, 1H, $J_{\text{H-H}} = 5.1$), 8.82 (d, 1H, $J_{\text{H-H}} = 4.8$), 7.94 (m, 2H), 7.73 (t, 1H, $J_{\text{H-H}} = 6$), 7.56 (d, 1H, $J_{\text{H-H}} = 6$), 7.33 (d, 1H, $J_{\text{H-H}} = 7.8$), 5.94 (m, 2H), 5.65 (d, 1H, $J_{\text{H-H}} = 6$), 5.48 (d, 2H, $J_{\text{H-H}} = 5.7$), 4.05 (s, 3H), 2.79 (m, 1H), 2.28 (s, 3H), 1.22 (dd, 6H, $J_{\text{H-H}} = 4.2, 13.7$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 173.26 (C-1), 156.33 (C-7), 154.28 (C-2), 150.84 (C-3), 147. (C-8), 138.81 (C-10), 137.82 (C-5), 129.41 (C-9), 128.66 (C-4), 125.79 (C-6), 125.24 (C-11), 106.76 (C, CPri), 101.83 (C, CMe), 87.67, 86.16, 85.10 (C, cymene ring), 51.07 (CH_3 , NCH_3), 31.42 (s, CH, CHMe_2), 22.05 (s, Me, CHMe_2), 18.88 (s, Me, CMe).

Complex **[2]PF₆**: 0.08 g (78%).

FTIR (KBr, cm^{-1}): 1645, 1523, 1460, 844.

^1H NMR: 9.43 (d, 1H, $J_{\text{H-H}} = 5.1$), 8.99 (d, 1H, $J_{\text{H-H}} = 4.8$), 8.83 (s, 1H), 8.02 (d, 1H, $J_{\text{H-H}} = 4.8$), 7.92 (s, 1H), 7.75 (s, 1H), 7.57 (s, 2H), 6.05 (s, 1H), 5.93 (s, 1H), 5.79 (s, 1H), 5.72 (s, 1H), 4.29 (qt, 2H), 2.80 (m, 1H), 2.34 (s, 3H), 1.48 (s, 3H), 1.19 (m, 6H).

2.3.2. Synthesis of $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{(\text{C}_5\text{H}_4\text{N})_2\text{C}=\text{NRi}\}\text{Cl}]\text{PF}_6\text{Cl}]\text{PF}_6$ {R = Me **[3]PF₆**, Et **[4]PF₆**}

A mixture of $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$ (0.048g, 0.072 mmol), 2,2'-dipyridyl-N-alkylimine (0.158 mmol) and NH_4PF_6 (0.025g, 0.158 mmol) were stirred in dry MeOH (20 ml) at room temperature for 6 hrs. An initially clear solution became increasingly cloudy as the reaction progressed. After stirring

for 6 hrs, the yellow solid was collected and washed with diethyl ether and dried under vacuum. More quantity of the compound was obtained by the rotary evaporation of the mother liquid and extraction with dichloromethane. The extract on concentration and addition of excess diethyl ether gave a bright orange yellow solid.

Yield and spectroscopic data are as follows:

Complex **[3]PF₆**: 0.076g (83%)

FTIR (KBr, cm⁻¹): 1645, 1539, 1394, 844.

¹HNMR: 8.97 (d, 1H, *J*_{H-H} = 5.7), 8.93 (d, 1H, *J*_{H-H} = 4.8), 8.80 (m, 1H), 8.39 (d, 1H, *J*_{H-H} = 8.1), 8.08 (m, 1H), 7.81 (m, 1H), 7.57 (d, 1H, *J*_{H-H} = 7.8), 7.38 (d, 1H, *J*_{H-H} = 9.3), 3.85 (s, 3H), 2.23 (d, 18H, *J*_{H-H} = 6).

¹³C {¹H} NMR (CDCl₃, δ): 175.01 (C-1), 155.24 (C-7), 153.24 (C-2), 150.29 (C-3), 148.48 (C-8), 138.82 (C-10), 138.53 (C-5), 130.31 (C-9), 129.03 (C-4), 126.96 (C-6), 125.45 (C-11), 95.32 (ring carbons, C₆Me₆), 48.70 (Me, NMe), 15.69 (Me, C₆Me₆).

Complex **[4]PF₆**:

0.081g (86%), 4hr, FTIR (KBr, cm⁻¹): 1699, 1460, 1396, 842.

¹HNMR: 8.96 (d, 1H, *J*_{H-H} = 4.5), 8.79 (d, 1H, *J*_{H-H} = 4.8), 8.38 (m, 2H), 8.11 (m, 2H), 7.77 (d, 1H, *J*_{H-H} = 6.3), 7.57 (m, 1H), 4.14 (qt, 2H, *J*_{H-H} = 7.2), 2.27 (s, 18H), 1.22 (t, 3H, *J*_{H-H} = 7.2).

2.3.3. Preparation of [(η⁶-C₆H₆)Ru{(C₅H₄N)₂C=NRi}Cl]PF₆ Cl]PF₆ {R = Me, **[5]PF₆**; Et, **[6]PF₆**}

A mixture of [(η⁶-C₆H₆)RuCl₂]₂ (0.05g, 0.106 mmol), NH₄PF₆ (0.0346g, 0.212 mmol) and excess of 2,2'-dipyridyl-N-alkylimine ligand (0.23 mmol) were stirred in MeOH (20 ml) for 7 hrs. Initially the suspension took a light muddy colour which turned into a dark brown colour as the reaction progressed. The solvent was removed under reduced pressure and the residue was extracted with dichloromethane and filtered. The filtrate on concentration to ca. 3 ml and addition of excess hexane induced a dark brown solid. The solid was washed with diethyl ether and hexane (2 x 10 ml) and dried in vacuum.

Yield and spectroscopic data are as follows:

Complex **[5]PF₆**: 0.078g (70%).

IR (KBr, cm⁻¹): 1645, 1523, 1460, 842.

¹HNMR (DMSO-d₆, δ): 9.71 (d, 1H, *J*_{H-H} = 6.1), 8.87 (d, 1H, *J*_{H-H} = 7.5), 8.22 (d, 1H, *J*_{H-H} = 8.1), 8.11 (m, 2H), 7.92 (d, 1H, *J*_{H-H} = 7.8), 7.72 (t, 1H, *J*_{H-H} = 8.3), 7.36 (t, 1H, *J*_{H-H} = 6.6), 6.18 (s, 6H, C₆H₆), 4.02 (s, 3H).

¹³C{¹H}NMR (DMSO-d₆, δ): 172.41 (C-1), 156.98 (C-7), 154.77 (C-2), 151.12 (C-3), 148.43 (C-8), 140.18 (C-10), 138.43 (C-5), 129.89 (C-9), 128.46 (C-4), 126.44 (C-6), 125.49 (C-11), 87.90 (ring C, C₆H₆), 51.27 (Me, NMe).

Complex **[6]PF₆**: 0.068g (60%).

IR (KBr, cm⁻¹): 1645, 1539, 1438, 844.

¹HNMR (DMSO-d₆, δ): 9.76 (d, 1H, *J*_{H-H} = 6), 8.83 (d, 1H, *J*_{H-H} = 4.8), 8.39 (d, 1H, *J*_{H-H} = 7.5), 8.07 (m, 2H), 7.96 (d, 1H, *J*_{H-H} = 6.8), 7.81 (m, 1H), 7.73 (d, 1H, *J*_{H-H} = 6.2), 6.18 (s, 6H), 4.02 (qt, 2H, *J*_{H-H} = 5.8), 1.35 (t, 3H, *J*_{H-H} = 9.4).

3. Structure analysis and refinement

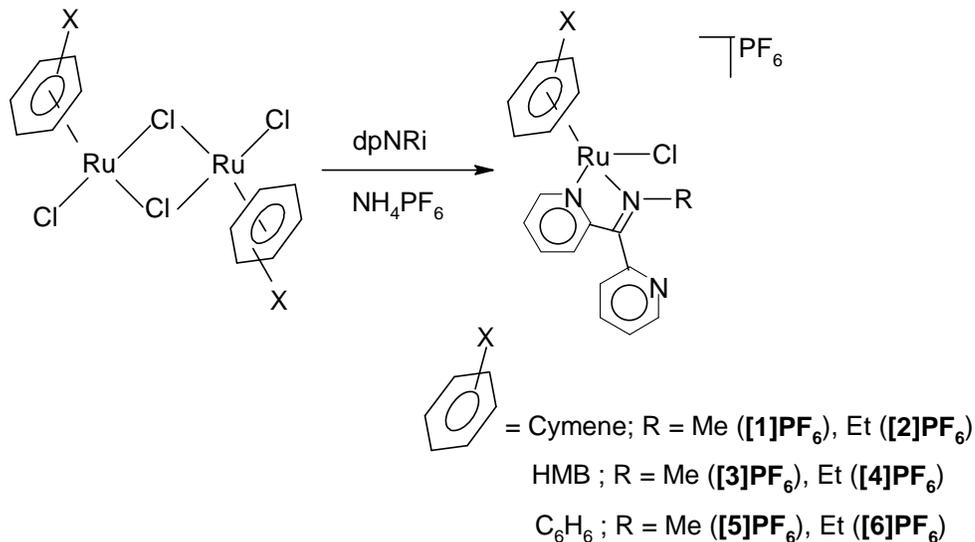
X-ray quality crystals of the complex **[3]PF₆** were grown by slow diffusion of hexane into dichloromethane solution of **[3]PF₆**. The X-ray diffraction data was collected at 296°K on a Nonius Kappa CCD FR590 single crystal X-ray diffractometer, using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Crystal-to-detector distance was 30 mm and exposure time was 15 seconds per degree. Data collection was 99.9% complete to 25° in θ . The data was integrated and scaled using hkl-SCALEPACK [23]. The structure was solved by direct methods (SHELXS, SIR97) [24] and refined by full matrix least squares base on F^2 using (SHELXL 97) [25]. The weighting scheme used was $W = 1/[\sigma^2(F^2_o) + 0.0490P^2 + 0.0000P]$ where $P = (F^2_o + 2F^2_c)/3$. All non hydrogen atoms were refined anisotropically while hydrogen atoms were placed in geometrically idealized positions and

constrained to ride on their parent atoms with C-H distances in the range 0.95-1.0 Å. Refinement converged at a final $R = 0.047$ (for observed data F), and $wR_2 = 0.1007$ (for unique data F^2).

4. Results and discussion

The reaction of $[\{(\eta^6\text{-arene})\text{RuCl}_2\}_2]$ with 2 fold excess of 2,2'-dipyridyl-N-alkylimine in the presence of NH_4PF_6 yielded the mononuclear complexes $[\mathbf{1}]\text{PF}_6$ - $[\mathbf{6}]\text{PF}_6$ as depicted in Scheme 2. These complexes are stable in air and isolated as their hexafluorophosphate salts with a 60-83% yield. All complexes are soluble in water, chlorinated solvents, and polar solvents such as methanol, acetonitrile etc. The complexes $[\mathbf{1}]\text{PF}_6$ - $[\mathbf{4}]\text{PF}_6$ are bright orange in colour while complexes $[\mathbf{5}]\text{PF}_6$ and $[\mathbf{6}]\text{PF}_6$ were dark brown. The complexes were characterized on the basis of FTIR, ^1H NMR and partly by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopic data.

It is noteworthy that in the case of complex $[\mathbf{1}]\text{PF}_6$, the reaction also yielded a minor quantity of complex $[\{(\eta^6\text{-cymene})\text{Ru}\}_2(\mu\text{Cl})_3]$ analogous to the compound $[\{(\eta^6\text{-C}_6\text{H}_6)\text{Ru}\}_2(\mu\text{Cl})_3]$ reported by Bennett *et al.*, from the reaction of $[\{(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2\}_2]$ with NH_4PF_6 in water [1]. It is believed that the compound's presence could be due to the residual water in the solvent. The compound was easily separated as red crystals from the mixture by slow diffusion of hexane into the dichloromethane solution of $[\mathbf{1}]\text{PF}_6$. The ^1H NMR of this compound showed two doublets at δ 5.50 and 5.65 assignable to the aromatic protons of *p*-cymene ring while protons of the isopropyl methyl appeared as a doublet at δ 1.31. The proton NMR spectra of complexes $[\mathbf{1}]\text{PF}_6$, $[\mathbf{3}]\text{PF}_6$ and $[\mathbf{5}]\text{PF}_6$ displayed a singlet resonance at around δ 4.02 assignable to methyl protons attached to nitrogen. Complexes $[\mathbf{2}]\text{PF}_6$, $[\mathbf{4}]\text{PF}_6$ and $[\mathbf{6}]\text{PF}_6$ displayed a triplet at around δ 1.22 and a quartet in the region of δ 4.02-4.29, assignable to the protons of methyl and methylene of the dpNeti ligand, respectively.



Scheme 2

Notably, the aromatic region of *p*-cymene ligand in the complex **[1]PF₆** displays an extra multiplet at δ 5.97 in addition to the usual two doublets observed at δ 5.87 and 5.71. This unusual pattern could be due to the long range coupling of diastereotopic methyl protons of isopropyl group and aromatic protons of the *p*-cymene ligand [27]. The isopropyl methyl groups are diastereotopic, since the ruthenium atom is stereogenic due to coordination of four different ligand atoms. Similar spectrum pattern has been reported in some other *p*-cymene ruthenium (II) complexes [27,28]. The methyl protons of the isopropyl group resonate at δ 1.22 as two set of doublets due to loss of planarity of the benzene ring [27]. The proton NMR spectra of all these complexes in the aromatic region of the pyridyl rings showed a similar spectrum pattern. The resonance of the *ortho* proton of the pyridine rings appeared as doublets at larger shifts in the region of δ 9.47-8.96 and δ 8.99-8.79 than those in the free ligands observed at around δ 8.74 and 8.53. This downfield in the chemical shifts is an indication of the cationic nature of the complexes. A similar downfield of chemical shifts was also observed for the alkyl protons attached to the nitrogen. For instant, the methyl proton of dpNmei was observed as a singlet at around δ 4.05 in the complexes **[1]PF₆**, **[3]PF₆** and **[5]PF₆** as

compared to the singlet resonance observed at δ 3.35 in the free dpNmei ligand. The complexes **[4]PF₆** and **[6]PF₆** displayed a quartet and triplet at around δ 4.02 and 1.22, respectively due to the resonance of methylene and methyl protons of the coordinated dpNeti ligand. However, in the case of *p*-cymene complex **[2]PF₆**, the resonance for methylene protons appeared as quartet at δ 4.29 and those for methyl protons of η^6 -*p*-cymene and dpNeti as singlet and broad multiplet at δ 1.16 and 1.48, respectively.

The electronic spectra of the complexes in dichloromethane exhibited absorption bands in the range 405-445 nm (Table 1). These low energy absorption bands are present in all these complexes could be a characteristic of Ru(d π)-L(π^*), metal to ligand charge transfer transition.

Table1. UV-visible data of the complexes in CH₂Cl₂ at room temperature

SL No.	Complexes	λ max (nm)
1	$[(\eta^6\text{-}p\text{-cymene})\text{Ru}\{(\text{C}_5\text{H}_4\text{N})_2\text{C}=\text{NMe}\}\text{Cl}]\text{PF}_6$ 1[PF₆]	447
2	$[(\eta^6\text{-}p\text{-cymene})\text{Ru}\{(\text{C}_5\text{H}_4\text{N})_2\text{C}=\text{NEt}\}\text{Cl}]\text{PF}_6$ 2[PF₆]	411
3	$[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{(\text{C}_5\text{H}_4\text{N})_2\text{C}=\text{NMe}\}\text{Cl}]\text{PF}_6$ 3[PF₆]	448
4	$[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{(\text{C}_5\text{H}_4\text{N})_2\text{C}=\text{NEt}\}\text{Cl}]\text{PF}_6$ 4[PF₆]	446
5	$[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}\{(\text{C}_5\text{H}_4\text{N})_2\text{C}=\text{NMe}\}\text{Cl}]\text{PF}_6$ 5[PF₆]	410
6	$[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}\{(\text{C}_5\text{H}_4\text{N})_2\text{C}=\text{NEt}\}\text{Cl}]\text{PF}_6$ 6[PF₆]	405

5. Crystal structure determination

The crystal structure determination was carried out for the representative complex **[3]PF₆**. The ORTEP diagram [29,30] of the complex including atom numbering scheme and PF₆ anion is shown in figure 1. Details of crystallographic data collection parameters are summarized in Table 2. Selected bond lengths and bond angles are listed in Table 3.

The complex **[3]PF₆** crystallized in space group P₁/2c. The geometry around the ruthenium atom can be regarded as pseudo octahedral with hexamethylbenzene occupying three coordination

sites in η^6 - fashion while the remaining coordination sites are occupied by chlorine and nitrogen atoms of coordinated ligand. The complex adopts the familiar “piano stool” structure as evident by the nearly 90° bond angles for N(1)-Ru(1)-Cl(1) ($86.12(9)^\circ$) and N(3)-Ru(1)-Cl(1) ($84.63(10)^\circ$). The ruthenium atom is π bonded to the hexamethylbenzene ring with an average Ru-C distance of $2.222(4) \text{ \AA}$, whereas average distance of ruthenium to the two chelating nitrogen atoms is 2.071 \AA . The two pyridyl rings of the dipyridyl ligand are not coplanar. The un-coordinated pyridyl ring is twisted out of the plane of the coordinated pyridyl ring with an angle $116.0(2)^\circ$. The bite angle of the chelating ligand N(1)Ru(1)-N(3) is $75.83(12)^\circ$, which is very close to that observed in the related complexes [27]. The average C-C bond length in the hexamethylbenzene ring is 1.414 \AA with alternating short and long bonds. Bonds C(1)-C(6), C(2)-C(3), C(4)-C(5) are shorter than C(1)-C(2), C(3)-C(4), C(5)-C(6) which could be due to the loss of planarity of the hexamethylbenzene ring. Similar patterns of alternate short and long C-C bonds of the hexamethylbenzene ring are reported in other hexamethylbenzene ruthenium complexes [27] and are indicative of a contribution from the cyclohexatriene resonance structures to the overall resonance hybrid [31].

Table 2. Summary of structure determination of complex [3]PF₆

Empirical formula	C ₂₄ H ₂₉ ClF ₆ N ₃ PRu
Formula Weight	640.22
Temperature (K)	295(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P2₁/c</i>
Unit cell dimensions	
<i>a</i> (Å)	10.2660 (2)
<i>b</i> (Å)	8.7525 (2)
<i>c</i> (Å)	30.6512 (8)
β (°)	107.1200 (8)
Volume (Å ³)	2632.07(10)
<i>Z</i>	4
Density (calculated) (Mg/m ³)	1.618
Absorption coefficient (mm ⁻¹)	0.819
F(000)	1296
θ range for data collection (°)	2.08-28.29
index ranges	$0 \leq h \leq 13$ $-11 \leq k \leq 0$ $-39 \leq l \leq 36$
Reflection collected/unique	36362/6207 [<i>R</i> _{int} = 0.057]
Completeness to theta	= 25°, 99.9%
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	6207 / 0 / 331
Goodness-of-fit on <i>F</i> ²	1.003
Final <i>R</i> indices	<i>R</i> ₁ = 0.0470; <i>WR</i> ₂ = 0.1007
[<i>I</i> > 2σ(<i>I</i>)]	
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1112; <i>WR</i> ₂ = 0.1332
Final different peak and hole (eÅ ⁻³)	0.622 and -0.747

Table 3. Selected bond lengths (Å) and bond angles (°) for complex [3]PF₆

<i>Bond lengths</i>			
Ru1-N1	2.080(3)	Ru1-N3	2.063(3)
N3-C18	1.283(5)	N3-C24	1.484(5)
Ru1-Cl	2.172(4)	N2-C19	1.294(6)
N1-C17	1.354(5)	C17-C18	1.457(5)
<i>Bond angles</i>			
N1-Ru1-N3	75.83(12)	N3-Ru1-Cl	84.63(10)
N2-C19-C18	116.5(4)	N1-C17-C18	113.9(3)
Ru1-N3-C18	118.9(3)	Ru1-N1-C17	116.0(2)
N3-C18-C19	123.9(4)	N3-C18-C17	114.9(3)

Conclusions

This paper described the synthesis of a series of water soluble (η^6 -arene) ruthenium (II) complexes bearing 2,2'-dipyridyl-N-alkylimine ligands. Spectral studies of the complexes and crystal structure of one of the representative complex [3]PF₆ are discussed showing structural features in accord with similar compounds. Synthesis of other arene ruthenium complexes bearing the 2,2'-dipyridyl-N-alkylimine ligand and other related dipyriddy ligands using an aprotic solvent such as acetonitrile is under way in our laboratory.

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Supplementary Materials

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre (CCDC), CCDC No. 764691 for this paper. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

References

- [1] M. A. Bennett, A. K. Smith, *J. Chem. Soc. Dalton Trans.* (1974) 233.
- [2] R. A. Zelonka, M. C. Baird, *Can. J. Chem.* 50 (1972) 3063.
- [3] D. R. Robertson, T. A. Stephenson, T. Arthur, *J. Organomet. Chem.* 162 (1978) 121.
- [4] H. Werner, R. Werner, *Chem. Ber.* 115 (1982) 3766.
- [5] Y. K. Yan, M. Melchart, A. Habtemariam, P. J. Sadler, *Chem. Commun.* (2005) 4764.
- [6] H. Chen, J. A. Parkinsons, S. Parsons, R. A. Coxall, R. O. Gould, P. J. Sadler, *J. Am. Chem. Soc.* 124 (2002) 3064.
- [7] C. S. Allardyce, P. J. Dyson, D. J. Ellis, S. L. Heath, *Chem. Commun.* (2001) 1396.
- [8] H. Horvath, G. Laurenczy, A. Katho, *J. Organomet. Chem.* 689 (2004) 1036.
- [9] K. S. Singh, V. Silvestik, P. Devi, Y. Mozharivskiy, *Inorg. Chim. Acta* 362 (2009) 5252.
- [10] J. Canivet, G. Labat, H. Stoekli-Evans, G. Suss-Fink, *Eur. J. Inorg. Chem.* (2005) 4493.
- [11] R. E. Morris, R. E. Aird, P. del S. Murdoch, H. Chen, J. Cummings, N. D. Hughes, S. Parsons, A. Parkin, G. Boyd, D. I. Jodrell, P. J. Sadler, *J. Med. Chem.* 44 (2001) 3616.
- [12] R. E. Aird, J. Cummings, A. A. Ritchie, M. Muir, R. E. Morris, H. Chen, P. J. Sadler, D. I. Jodrell, *Br. J. Cancer* 86 (2002) 1652.
- [13] V. Tangoulis, C. P. Raptopoulou, A. Terzis, S. Pachalidou, S. P. Perlepes, E. G. Bakalbassis, *Inorg. Chem.* 36 (1997) 3996.
- [14] A. C. Deveson, S. L. Hearth, C. J. Harding, A. K. Powell, *J. Chem. Soc. Dalton Trans.* (1996) 3173.
- [15] M. Haukka, P. D. Costa, S. Luukkanaen, *Organometallics* 22 (2003) 5137.
- [16] M. J. Rauterkus, S. Fakih, C. Mock, I. Pascasu, B. Krebs, *Inorg. Chim. Acta* 350 (2003) 355.
- [17] J.F. Berry, F. A. Cotton, L.M. Daniels, C. a. Murillo, X. Wang *Inorg. Chem.* 42 (2003) 2418.

- [18] J. A. Cabeza, I. del Rio, S. Gracis-Granda, V. Riera, M. Saurez, *Organometallics* 21 (2002) 2540.
- [19] S. Kar, N. Chanda, S.M. Mobin, F. A. Urbanos, M. Niemeyer, V. G. Puranik, R. Jimenez-Aparico, G.K. Lahiri, *Inorg. Chem.* 44 (2005) 1571.
- [20] M. A. Benette, T. W. Matheson, G. B. Robertson, A. K. Smith, P. A. Tucker, *Inorg. Chem.* 19 (1980) 1014.
- [21] M. A. Benette, T. N. Huang, T. W. Matheson, A.K. Smith, *Inorg. Synth.* 21 (1985) 75.
- [22] B. Flores-Chavez, B. A. Martinez-Ortega, J. G. Alvarado-Rodriguez, N. Andrade-Lopez, *J. Chem. Cryst.* 35 (2005) 2219.
- [23] Z. Otinowski, W. Minor, Processing of X-ray Diffraction Data Collected in Oscillation Mode, *Methods in Enzymology*, 276 (1996) 307, C. W. Carter, Jr.R. M. Sweet, Eds. Academic Press.
- [24] SIR97: A. Altomare, G. Cascarano, C. Giacovazzo, M.C. Burla, G. Polidori, M. Camalli, *J. Appl. Cryst.* 27 (1994) 435.
- [25] G.M. Sheldrick, (1997) SHELXL97, *Program for the Refinement of Crystal Structures*, University of Gottingen, Germany.
- [26] T. Arthur, T. A. Stephenson, *J. Organomet. Chem.* 208 (1981) 369.
- [27] R. Lalrempuia, M. R. Kollipara, P. J. Carroll, *Polyhedron* 22 (2003) 605.
- [28] K. T. Prasad, B. Therrien, K. M. Rao, *J. Organomet. Chem.* 693 (2008) 3049.
- [29] maXus: S. MacKay, C. J. Gilmore, C. Edwards, M. Tremayne, N. Stewart, K. Shankland, 1998 "maXus: a computer program for the solution and refinement of crystal structures from diffraction data" University of Glasgow, Scotland, U. K., Nonius B.V, Delft, The Netherlands and MacScience Co. Ltd., Yokohama, Japan.
- [30] Zortep: L. Zsolnai, G. Huttner, 1994 *University of Heidelberg*.
- [31] P. Laruerta, J. Latorre, M. Sanau, F. A. Cotton, W. Schwotzer, *Polyhedron* 7 (1988) 1311.

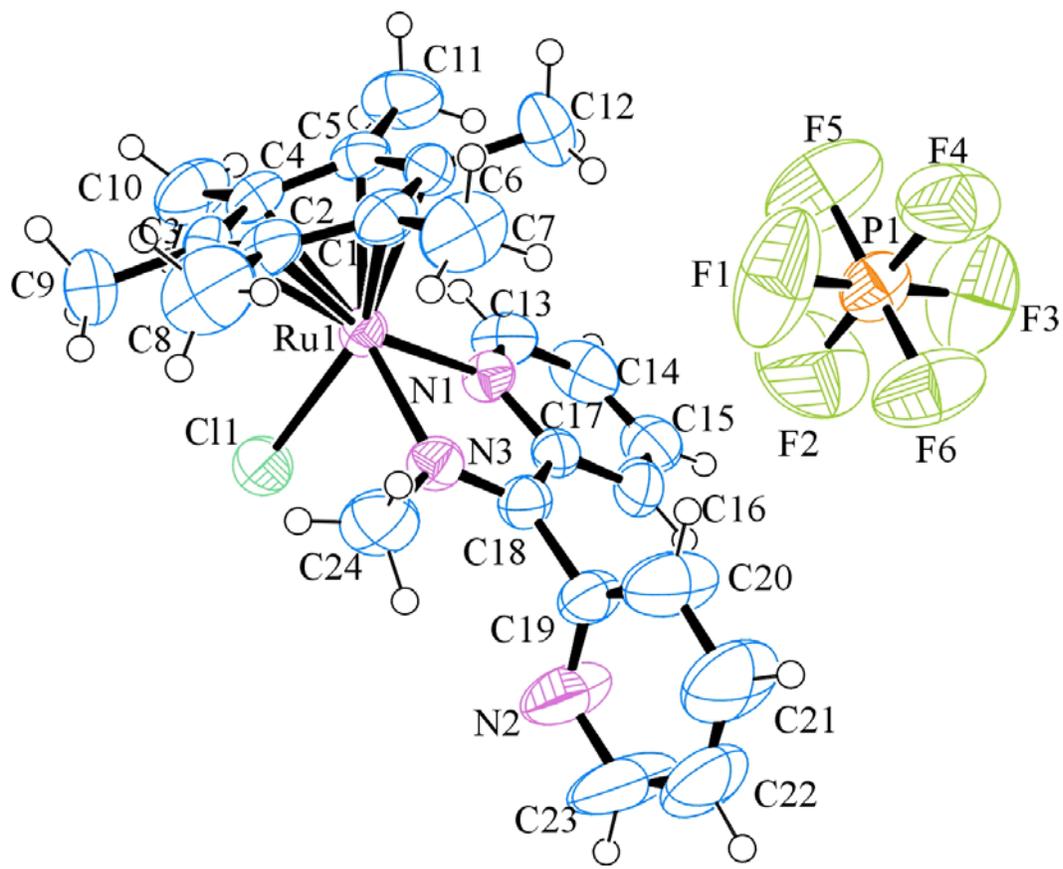


Figure1. ORTEP diagram of [3]PF₆. Thermal ellipsoids are drawn at the 50% probability level.