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Reactivity studies of η^6-arene ruthenium (II) dimers with polypyridyl ligands: isolation of mono, binuclear *p*-cymene ruthenium (II) complexes and bisterpyridine ruthenium (II) complexes

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Abstract

The complexes $[(\eta^6\text{-}p\text{-cymene})RuCl(L_2)]^+$ where $L_2 = 2,2'$-biquinoline (biqui) (**3**), 2,9-dimethyl 4,7-diphenyl-1,10-phenanthroline (ddp) (**4**), and 2,3-bis(α-pyridyl) quinoxaline (bpq) (**5**) were obtained by halide bridge cleavage of $[\{(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}Cl)\}_2Cl_2]$ (**1**) with the corresponding ligands. The ligand bridged binuclear compound $[\{(\eta^6\text{-cymene})RuCl\}_2(bpq)]^{2+}$ (**6**) was also obtained by treating **1** with stoichiometric amount of bpq in methanol. The reactions of $[\{(\eta^6\text{-arene})Ru(\mu\text{-}Cl)\}_2Cl_2]$, {arene = *p*-cymene (**1**), hexamethylbenzene (**2**)} with substituted phenylterpyridines (x-phterpy, x = H, CH_3, OCH_3) yielded bis terpyridine complexes of the type $[(x\text{-phterpy})_2Ru]^{2+}$ by the facile displacement of η^6-arene ring as well as chloride ligands. These complexes were characterized by FT-NMR, FT-IR spectroscopy, and analytical data. The molecular structures of $[(\eta^6\text{-}p\text{-cymene})RuCl(biqui)]PF_6$ (**3**) and $[(\eta^6\text{-}p\text{-cymene})RuCl(bpq)]PF_6$ (**5**) have been determined by single crystal X-ray diffraction study.

Keywords: *p*-Cymene; Hexamethylbenzene; Ruthenium; Terpyridine; 2,2′-Biquinoline; 2,9-Dimethyl; 4,7-Diphenyl-1; 10-Phenanthroline; 2,3-Bis(α-pyridyl)quinoxaline

1. Introduction

The arene ruthenium complexes played an important role in organometallic chemistry. Synthesis of half sandwich ruthenium (II) complexes received considerable attention owing to their catalytic properties [1] and water-soluble half-sandwich arene ruthenium (II) complexes have shown interesting anti-tumor activity [2].

It has been previously reported the reactivity of terdenate polypyridyl ligands toward cyclopentadienyl, indenyl, and pentamethylcyclopentadienyl ruthenium systems where η^5-bonded moieties remain intact and thus forming $[(\eta^5\text{-Ar})Ru(terpy)(PPh_3)]^+$, (Ar = C_5H_5, C_9H_7, C_5Me_5) [3] or $[(\eta^5\text{-}C_5Me_5)MCl(phterpy)]^+$ (M = Rh, Ir) [4], however, the reaction of these ligands with the isolectronic halide bridged arene ruthenium complexes of the type $[\{(\eta^6\text{-arene})Ru(\mu\text{-}Cl)\}_2Cl_2]$, (arene = *p*-cymene, hexamethylbenzene), does not form the expected $[(\eta^6\text{-arene})RuCl(phterpy)]^+$ but instead irrespective of the solvents used gave only known bis terpyridine ruthenium complexes [5]. This observation prompted us to investigate the reactivity of $[\{(\eta^6\text{-arene})Ru(\mu\text{-}Cl)\}_2Cl_2]$, with more steric and bulkier chelating *N*,*N*′-heterocycles. Initial studies of these complexes with 2,2′-bipyridine and 1,10-phenanthroline have been reported [6].

In this paper, we would like to report the formation of $[(\eta^6\text{-arene})RuCl(L_2)]^+$ complexes and also the facile displacement of η^6-bonded arene as well as the chloride ligands by phenylterpyridines from $[\{(\eta^6\text{-arene})Ru(\mu\text{-}Cl)\}_2Cl_2]$ forming known complexes of the type $[(phterpy)_2Ru]^{2+}$. In order to confirm the nature of bonding, the structures of $[(\eta^6\text{-}p\text{-cymene})RuCl(biqui)]PF_6$ and $[(\eta^6\text{-}p\text{-cymene})RuCl(bpq)]PF_6$ have been solved by X-ray crystallography.

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2. Experimental

All chemicals used were of reagent grade. All reactions were carried out in purified and dried solvents. ^{1}H NMR spectra were recorded on a Bruker ACF 300 spectrometer. Infrared spectra were taken on a Perkin–Elmer model 983 spectrophotometer using CsI pellets. Elemental analysis was performed in Perkin–Elmer-2400 CHN analyzer. [{(η^6-arene)Ru(μ-Cl)}$_2$Cl$_2$] [7], 2,3-bis(α-pyridyl) quinoxaline [8], 4′-phenyl-2,2′:6′,2″-terpyridine (phterpy) [9], 4′-*p*-methylphenyl-2,2′:6′,2″-terpyridine (Me-phterpy), and 4′-*p*-methoxyphenyl-2,2′:6′,2″-terpyridine (OMe-phterpy) [10] were prepared according to the procedure described in the literature.

2.1. Preparation of [(η^6-cymene)Ru(biqui)Cl]PF$_6$ (**3**)

The mixture of [{(η^6-*p*-cymene)Ru(μCl)}$_2$Cl$_2$] (0.05 g, 0.081 mmol), 2,2′-biquinoline (0.055 g, 0.214 mmol), and NH_4PF_6 (0.080 g, 0.488 mmol) excess was stirred in a mixture of methanol (10 ml) and CH_2Cl_2 (10 ml) at room temperature for 1.5 h and the solvents were removed under reduced pressure. The residue was redissolved in acetone and filtered to remove the insoluble precipitated NH_4Cl. The volume was reduced to about 2 ml; addition of excess hexane gave yellow compound. Single crystals were grown by slow evaporation of acetonitrile solution. Yield: 0.155 g, 70.76%. *Anal.* Calc. for $C_{28}H_{26}ClN_2F_6PRu$: C, 50.04; H, 3.90; N, 4.16. Found C, 50.10; H, 3.94; N, 4.19%. ^{1}H NMR (δ, CD_3CN): 8.94 (d, $J = 8.7$ Hz), 8.59 (d, $J = 8.4$ Hz), 8.40 (d, $J = 8.4$ Hz), 8.11 (m), 7.91 (t, $J = 7.5$ Hz), 5.72 (d, $J = 6$ Hz), 5.57 (d, $J = 6$ Hz), 2.31 (s), 0.79 (d, $J = 6.9$ Hz). IR (CsI, cm^{-1}): 844 (s, ν_{P-F}), 557 (s), 310 (m, ν_{Ru-Cl}).

2.2. Preparation of [(η^6-*p*-cymene)Ru(ddp)Cl]PF$_6$ (**4**)

The mixture of [{(η^6-*p*-cymene)Ru(μCl)}$_2$Cl$_2$] (0.074 g, 0.122 mmol), 2,9-dimethyl, 4,7-diphenyl-l,10-phenanthroline (ddp) (0.088 g, 0.244 mmol), and NH_4PF_6 (0.080 g, 0.488 mmol) in methanol (20 ml) was stirred at room temperature for 2 h. Then the solvent was removed under reduced pressure, the residue was redissolved in acetone, and then filtered to remove the insoluble NH_4Cl. The volume was reduced to about 2 ml and addition of excess hexane gave a yellow product. Yield: 0.150 g, 59.19%. *Anal.* Calc. for $C_{36}H_{34}N_2Cl\,F_6PRu$: C, 61.90; H, 3.89; N, 3.60. Found C, 62.04; H, 3.90; N, 3.69%. ^{1}H NMR (δ, $CD_3CN + CDCl_3$): 8.06 (s), 7.86 (s), 7.62 (m), 5.83–5.50 (m), 3.09 (s), 2.86 (sept), 2.24 (s), 1.32 (dd, $J = 3.6$ Hz). IR (CsI, cm^{-1}): 844 (s, ν_{P-F}), 558 (s), 306 (m, ν_{Ru-Cl}).

2.3. Preparation of [(η^6-*p*-cymene)RuCl(bpq)]PF$_6$ (**5**)

The mixture of [{(η^6-*p*-cymene)Ru(μCl)}$_2$Cl$_2$] (0.1 g, 0.163 mmol), 2,3-bis(α-pyridyl)quinoxaline (0.098 g, 0.347 mmol), and NH_4PF_6 (0.061 g, 0.376 mmol) was refluxed in 10 ml of methanol under dry nitrogen atmosphere for 1 hour. The resulting solution was filtered to remove insoluble brown product. The filtrate was then evaporated under vacuum on a rotary evaporator, the residue was redissolved in CH_2Cl_2 and filtered, the volume was reduced to about 2 ml, then excess hexane was added which gave an oily product. It was washed several times with hexane to give orange-red microcrystalline solid. Suitable crystals for X-ray structure determination were grown by slow diffusion of hexane into acetone solution. Yield: 0.152 g, 66.6%. UV–Vis (CH_3CN, 1×10^{-3} M): λ_{max} 392 nm. *Anal.* Calc. for $C_{28}H_{26}ClF_6N_4PRu$: C, 48.04; H, 3.74; N, 7.99. Found C, 48.14; H, 3.90; N, 8.04%. ^{1}H NMR {δ, $(CD_3)_2CO$}: 9.55 (d, $J = 1.5$ Hz), 8.99 (d, $J = 2.4$ Hz), 8.67 (t, $J = 1.5$ Hz) 8.42–8.15 (m), 8.02 (t, $J = 6$ Hz), 7.80–7.70 (m), 7.3 (d, $J = 1.8$ Hz), 6.44 (d, $J = 6.6$ Hz), 6.28 (d, $J = 6.6$ Hz), 6.12 (d, $J = 5.1$ Hz), 2.60 (sept), 2.42 (s), 1.15 (d, $J = 7.2$ Hz), 1.07 (d, $J = 6.9$ Hz). IR (CsI, cm^{-1}): 844 (s, ν_{P-F}), 557 (s), 304 (br, m, ν_{Ru-Cl}).

2.4. Preparation of [{(η^6-*p*-cymene)RuCl}$_2$(bpq)](PF$_6$)$_2$ (**6**)

2.4.1. Method (i)

The brown insoluble product from the preparation of complex **5** was dissolved in acetone to give a violet color solution, which was reduced to a few ml and addition of diethylether gave the complex **6**.

2.4.2. Method (ii)

The mixture of [{(η^6-*p*-cymene)Ru(μCl)}$_2$Cl$_2$] (0.1 g, 0.163 mmol), 2,3-bis(pyridyl)quinoxaline (0.046 g, 0.163 mmol), and NH_4PF_6 (0.06 g, 0.373 mmol) was refluxed in methanol (10 ml). Violet color precipitate appears after 15 min and the whole reaction mixture was refluxed for 1 h. The reaction mixture was cooled to room temperature and filtered; the precipitate was washed several times with water and then with methanol and then finally with diethylether to give dark violet shiny product. It was air-dried. Yield: 0.160 g, 87.91%. *Anal.* Calc. for $C_{38}H_{40}C_{12}N_4P_2F_{12}Ru_2$: C, 40.91; H, 3.58; N, 5.02. Found C, 41.12; H, 3.60; N, 5.13%. UV–Vis (CH_3CN, 1×10^{-3} M): $\lambda_{max:}$ 463 nm. ^{1}H NMR {δ, $(CD_3)_2CO$}: 9.44 (d, $J = 6$ Hz), 8.88 (m), 8.48 (d, $J = 8.1$ Hz), 8.41 (m), 8.15 (t, $J = 8.1$ Hz), 7.90 (t, $J = 6.6$ Hz), 6.19 (d, $J = 6.3$ Hz), 6.10 (d, $J = 6.3$ Hz), 5.87 (t, $J = 5.7$ Hz), 2.75 (sept), 2,23 (s), 1.20 (d, $J = 6.9$ Hz), 1.09 (d, $J = 6.9$ Hz). IR (CsI, cm^{-1}): 844 (s, ν_{P-F}), 557 (s), 306 (m, ν_{Ru-Cl}).

2.5. Preparation of [{(η^6-C_6Me_6) Ru(μ-Cl)}$_2$Cl$_2$]

The mixture of [{(η^6-*p*-cymene)Ru(μ-Cl)}$_2$Cl$_2$] (0.13 g, 0.21 mmol) and hexamethylbenzene (1.3 g, 0.21 mmol) was refluxed in diglyme (18 ml) with stirring under dry nitrogen atmosphere for around 9 h. The

solution was cooled to room temperature and the red brown product was filtered off, washed with hexane (5×10 ml) to remove excess hexamethylbenzene and *p*-cymene dimer and finally with diethylether. The compound was recrystallized from chloroform/diethylether. Yield: 0.026 g, 18.5%. ^{1}H NMR ($CDCl_3$): δ 2.02 (s) [lit [7(b)]: 2.03]. ^{13}C NMR ($CDC1_3$): δ 89.61 (s), δ 15.92 (s). IR (CsI, cm^{-1}): 297 (s), 259 (s) [lit [7(b)]: 299, 258].

2.6. η^6-Arene displacement reactions

The mixture of $[\{(\eta^6\text{-arene})Ru(\mu\text{-Cl})\}_2Cl_2]$ (arene = *p*-cymene, hexamethylbenzene) (0.163 mmol), phenylterpyridine ligands (0.407 mmol), and NH_4BF_4 (0.489 mmol) was stirred in dry methanol (15 ml) at room temperature, the color of the solution immediately changed to purple, stirred for 2 h whereby red brown compound was precipitated out. The solvent was slowly removed in rotary evaporator. The residue was redissolved in acetone and filtered to remove any insoluble materials. Acetone solution was reduced to about 2 ml and addition of excess hexane precipitated out red brown compound.

1. $[(phterpy)_2Ru](BF_4)_2$. Yield: 0.120 g, 41.09% (from **1**), UV–Vis(1×10^{-3} M, CH_3CN): λ_{max} 489 nm. *Anal.* Calc. for $C_{42}H_{30}BF_4N_6Ru$: C, 56.48; H, 3.35; N, 9.45. Found C, 56.52; H, 3.40; N, 9.49%. ^{1}H NMR {δ, $(CD_3)_2CO$}: 9.46 (2H, s), 9.11 (2H, d, $J = 8.1$ Hz), 8.36 (2H, dd, $J = 1.2$ Hz), 8.14 (3H, dt, $J = 1.2$ Hz), 7.85–7.69 (4H, m), 7.38 (2H, dt, 1.2 Hz).
2. $[(Me\text{-}phterpy)_2Ru](BF_4)_2$. Yield: 0.125 g, 41.66% (from **1**), UV–Vis(1×10^{-3} M, CH_3CN): λ_{max} 480 nm. *Anal.* Calc. for $C_{44}H_{34}BF_4N_6Ru$: C, 57.35; H, 3.68; N, 9.16. Found C, 57.39; H, 3.72; N, 9.2%. ^{1}H NMR {δ, $(CD_3)_2$ CO}: 9.43 (2H, s), 9.08 (2H, d, $J = 8.1$ Hz), 8.29 (2H, d, $J = 8.7$ Hz), 8.11 (2H, dt, $J = 1.2$ Hz), 7.82 (2H, dd, $J = 1.2$ Hz), 7.58–7.36 (4H, m), 2.52 (3H, s).
3. $[(OMe\text{-}phterpy)_2Ru](BF_4)_2$. Yield: 0.127 g, 40.83% (from **1**), UV–Vis(1×10^{-3} M, CH_3CN): λ_{max} 482 nm. *Anal.* Calc. for $C_{40}H_{34}BF_4N_6O_2Ru$: C, 55.42; H, 3.56; N, 8.85. Found C, 55.48; H, 3.60; N, 8.91%. ^{1}H NMR {δ, $(CD_3)_2CO$}: 9.40 (2H, s), 9.07 (2H, d, $J = 8.1$ Hz), 8.36 (2H, d, $J = 8.7$ Hz), 8.08 (2H, dt, 1.2 Hz), 7.82 (2H, dd, $J = 0.9$ Hz), 7.36–7.28 (4H, m), 3.99 (3H, s).

2.7. Crystal structure determination of **3** and **5**

A suitable size crystal was mounted on the end of the glass fiber and mounted on a Nonius MACH3 diffractometer with graphite monochromatized Mo Kα ($\lambda = 0.70930$ Å) radiation at a temperature of 293 K for the cell determination and intensity data collection. Crystal data collection parameters are summarized in Table 1. All crystallographic calculations were performed with the use of the Maxus [11] software. The structure was solved by direct methods [12] (SHELXS 1997). Refinement was by full-matrix least squares based on F^2 using SHELXL-93 [13]. Lorentz and polarization corrections were applied. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a ''riding'' model. Figs. 1 and 2 are the ORTEP [14] representation of the molecules with 50% probability thermal ellipsoids displayed. Selected bond distances and angles are given in Tables 2 and 3 for complexes **3** and **5**, respectively.

3. Results and discussion

The cationic mono nuclear complexes with the general formulation $[(\eta^6\text{-}p\text{-cymene})RuCl(L_2)]^+$, $L_2 = 2,2$-biqui, ddp and bpq were prepared by the reaction of $[\{(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-Cl})\}_2Cl_2]$ with excess of L_2 in methanol however, addition of dichloromethane as a co-solvent is necessary to prepare complex **3**. These complexes are soluble in acetone, acetonitrile, and DMSO

$$[\{(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-Cl})\}_2Cl_2] \xrightarrow{L2} [(\eta^6\text{-}p\text{-cymene})RuCl(L_2)]^+$$

$L_2 = 2,2'$-biquinoline (2,2′-biqui) (**3**), 2,9-dimethyl 4,7-diphenyl-phenanthroline (ddp) (**4**), 2,3-bis(α-pyridyl)quinoxaline (bpq) (**5**).

The reaction of *p*-cymene dimer with two and half fold excess of bpq in methanol in refluxing condition yielded two compounds, the ^{1}H NMR spectrum of the main product showed unsymmetrical splitting pattern of the bpq ligand in aromatic region which suggests the compound to be a mononuclear complex $[(\eta^6\text{-}p\text{-cymene})RuCl(bpq)]^+$ (**5**). The byproduct, which could also be isolated from the reaction between *p*-cymene dimer and bpq in 1:1 molar ratio, showed six distinct peaks in the aromatic region apart from the characteristic signals for the *p*-cymene moiety. The integration of the spectrum suggests the compound to be binuclear ligand bridged compound of the formula $[\{(\eta^6\text{-}p\text{-cymene})RuCl\}_2(bpq)](PF_6)_2$ (**6**) as shown below.

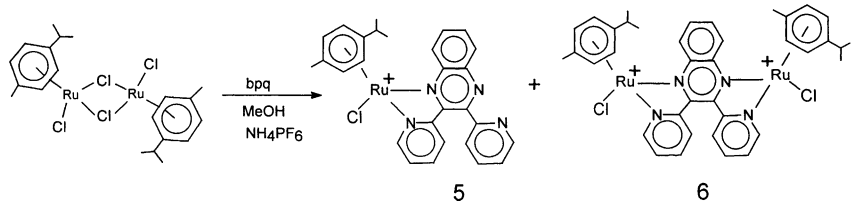


Table 1
Summary of structure determinations of compounds **3** and **5**

	Complex **3**	Complex **5**
Empirical formula	$C_{28}H_{26}ClF_6N_2PRu$	$C_{28}H_{26}ClF_6N_4PRu$
Formula weight	671.99	700.02
Temperature (K)	293 (2)	293 (2)
Wavelength (Å)	0.70930	0.70930
Crystal system, space group	monoclinic, *P*21/*n*	monoclinic, *P*21/*n*
Unit cell dimensions		
a (Å)	12.47 (5)	9.9920 (11)
b (Å)	15.22 (5)	16.3600 (15)
c (Å)	13.96 (5)	17.6190 (12)
β (°)	94.3 (2)	95.406 (7)
Volume (Å^3)	2641 (17)	2867.4 (5)
Z, D_{calc} (M g/m^3)	4, 1.687	4, 1.622
Absorption coefficient (mm^{-1})	0.820	0.761
F(000)	1348	1408
Crystal size (mm)	0.4 × 0.35 × 0.35	0.35 × 0.20 × 0.15
θ Range for data collection (°)	1.98–24.92	1.70–24.93
Index ranges	$0 \leqslant h \leqslant 14$, $0 \leqslant k \leqslant 18$, $-16 \leqslant l \leqslant 16$	$0 \leqslant h \leqslant 11$, $0 \leqslant k \leqslant 19$, $-20 \leqslant l \leqslant 20$
Reflections collected/unique	4041/4041 [*R*(int) = 0.0000]	4272 / 4272 [*R*(int) = 0.0000]
Completeness to 2*θ* =	24.92–83.8%	24.93–81.7%
Absorption correction	Psi-scan	Psi-scan
Maximum and minimum transmission	1.000 and 0.797	1.000 and 0.904
Refinement method	full-matrix least-squares F^2	
Data/restraints/parameters	4041/0/352	4272/0/450
Goodness-of-fit on F^2[a]	1.653	1.059
Final *R* indices [$I > 2\sigma(I)$][b]	$R_1 = 0.1313$, $wR_2 = 0.3402$	$R_1 = 0.0457$, $wR_2 = 0.1088$
R indices (all data)	$R_1 = 0.1444$, $wR_2 = 0.3600$	$R_1 = 0.0618$, $wR_2 = 0.1203$
Largest differential peak and hole (e Å^{-3})	4.278 and −2.858	0.659 and −0.558

[a] $GOF = \{\sum w(F_o^2 - F_c^2)^2/(n-p)\}^{1/2}$, where n = the number of reflections and p = the number of parameters refined.
[b] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ $wR_2 = \{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\}^{1/2}$.

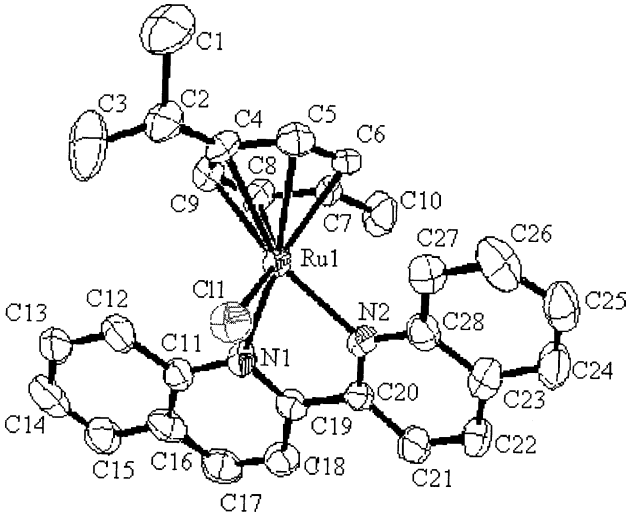


Fig. 1. ORTEP drawing of the compound **3** with 50% probability thermal ellipsoids. Hydrogen atoms and PF_6 omitted for clarity.

The ^{1}H NMR spectra of the complexes **4** and **5** exhibited the resonance of the methyl protons of isopropyl group as two doublets at around 1.32 and 1.13

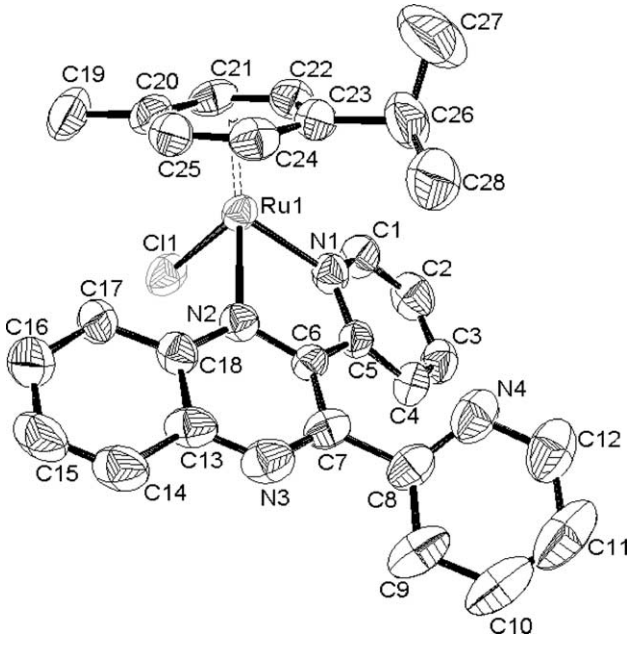


Fig. 2. ORTEP drawing of the compound **5** with 50% probability thermal ellipsoids. Hydrogen atoms and PF_6 omitted for clarity.

Table 2
Bond lengths [Å] and angles [°] for [(η^6-cymene)Ru(biqui)Cl]PF_6 (**3**)

Bond lengths			
Ru(1)–N(1)	2.101(12)	Ru(1)–N(2)	2.126(10)
Ru(1)–C(8)	2.157(15)	Ru(1)–C(6)	2.174(13)
Ru(1)–C(7)	2.193(14)	Ru(1)–C(5)	2.196(14)
Ru(1)–C(9)	2.210(14)	Ru(1)–C(4)	2.243(14)
Ru(1)–Cl(1)	2.388(8)	C(4)–C(9)	1.371(19)
C(4)–C(5)	1.392(18)	C(5)–C(6)	1.395(18)
C(6)–C(7)	1.395(19)	C(7)–C(8)	1.432(17)
C(8)–C(9)	1.412(17)		
Bond angles			
N(1)–Ru(1)–N(2)	76.6(4)		
N(2)–Ru(1)–Cl(1)	86.4(3)		
N(1)–Ru(1)–Cl(1)	87.8(3)		

Table 3
Selected bond lengths [Å] and angles [°] for [(η^6-cymene)Ru(bpq)Cl]PF_6 (**5**)

Bond lengths		Bond angles	
Ru(1)–N(1)	2.059(4)	N(1)–Ru(1)–N(2)	76.17(17)
Ru(1)–N(2)	2.089(4)	N(1)–Ru(1)–Cl(1)	84.61(13)
Ru(1)–C(20)	2.239(6)	N(2)–Ru(1)–Cl(1)	87.67(13)
Ru(1)–C(21)	2.183(6)		
Ru(1)–C(22)	2.184(6)		
Ru(1)–C(23)	2.194(6)		
Ru(1)–C(24)	2.165(6)		
Ru(1)–C(25)	2.208(6)		
Ru(1)–Cl(1)	2.3804(15)		
C(20)–C(21)	1.423(9)		
C(20)–C(25)	1.376(9)		
C(21)–C(22)	1.395(9)		
C(22)–C(23)	1.428(9)		
C(23)–C(24)	1.391(9)		
C(24)–C(25)	1.409(9)		

ppm, respectively, and more than two sets of doublets for the *p*-cymene ring protons at around 6 ppm which could be due to loss of planarity of the cymene ring because of steric ligands. This splitting pattern is solely due to the nature of the incoming ligands. Complex **3** exhibited the resonance of methyl protons of the isopropyl group as a doublet at 0.79 ppm and *p*-cymene ring protons appeared as two sets of doublet at 5.72 and 5.57 ppm, respectively. The far infrared spectra of these complexes showed bands at around 304–310 cm^{-1}, which were assigned to terminal $\nu_{(Ru-Cl)}$ stretching vibrations, these values are slightly higher compared to the values observed for the closely related complexes [6].

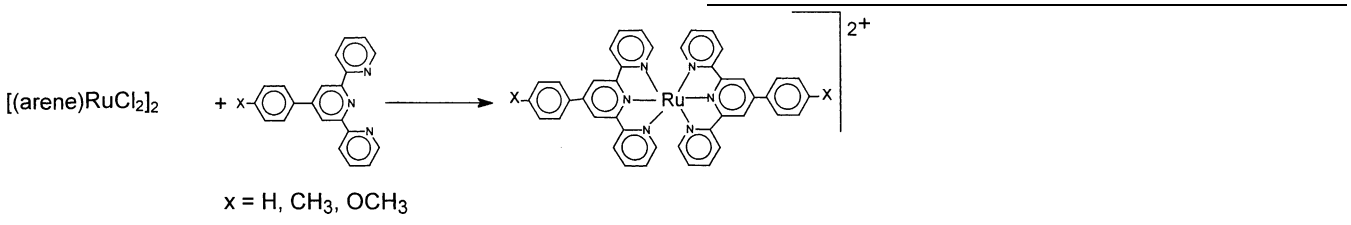
It was observed that the MLCT band of complex **6** shows considerable red shift compared to the mononuclear complex **5**. The red shift in the position of Ru → bpq CT transition towards lower energy may result from the stabilization of bpq π^* orbital upon coordination to the second ruthenium center [15].

The complex [{(η^6-C_6Me_6)Ru(μ-Cl)}$_2$$Cl_2$] (**2**) was also prepared by the arene displacement reaction starting from *p*-cymene dimer with hexamethylbenzene in refluxing diethylene glycol dimethyl ether (diglyme). The literature method sometimes resulted in the decomposed product. The desired compound was successfully isolated but in unrepeatable low yield.

Terpyridines in principle can bind metals in bidentate fashion leaving one pyridyl ring uncoordinated [3,4] and also as monodentate or tridentate or as bridging ligand. The reaction of complex **1** with stoichiometric or excess amount of para substituted phenylterpyridines in different solvents viz, acetonitrile, benzene, chloroform, ethanol, methanol, and diethylether at room temperature or refluxing condition resulted only in the facile displacement of the *p*-cymene ring as well as the chloride ligands. The ^{1}H NMR data, far IR spectra suggested the absence of *p*-cymene ring and halide ligand in these complexes and analytical data indicated the products as a well known dicationic complexes of the type [(x-phterpy)$_2$ Ru]$^{2+}$. The reaction between these ligands and **2** also resulted in the similar products.

3.1. Crystal structure

Single crystal X-ray structure determinations were carried out for complexes **3** and **5** (Figs. 1 and 2) for confirmation of the formulation. However, the low accuracy of the result from **3** would render a discussion of the metrical parameters meaningless. The data collection parameters are listed in Table 1 and bond lengths and bond angles are listed in Tables 2 and 3. The ruthenium atom is bonded to the two nitrogen atoms of the ligand, one chloride ligand and to a *p*-cymene group through the



six carbon atoms. The geometry about the metal atom can be regarded as distorted octahedral if the η^6-cymene group is assumed to occupy three facial coordinated positions. In complex **5**, the average Ru–C bond length is 2.195 Å with Ru–C(20) and Ru–C(25) bond distances slightly longer than the rest. The average C–C distance is 1.399 Å with alternate short and long bond length.

The Ru–Cl(1) bond length is 2.3804 Å, which falls within the usual range of Ru–Cl bond distance [16]. The bite angle of the chelating ligand is 76.12°(17). The two Ru–N bond lengths are slightly different (2.059 and 2.089 Å). The bond angles of N(1)–Ru–Cl(1) and N(2)–Ru–Cl(1) are 84.61(3)° and 87.67(3)°, respectively, indicating the three legged piano stool type structure of the compound.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre (CCDC), CCDC No. 196366 for complex **3** and 209301 for complex **5**. 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 www: http://www.ccdc.cam.ac.uk).

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