

# Syntheses and Structures of Two Arene-Ruthenium(II) Complexes with Cyclometalating 2-Pyridyl-*m*-tolyl Ligands

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Reactions of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$  and  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$  with  $[\text{Hg}(\text{ptpy})_2]$  ( $\text{Hptpy}$  = 2-pyridyl-*m*-toluene) in THF afforded  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{ptpy})_2(\mu\text{-Hg}_2\text{Cl}_6)]$  **1** and  $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{ptpy})_2(\mu\text{-Hg}_2\text{Cl}_6)]$  **2**, respectively. The crystal structures of complexes **1** and **2** have been determined by single-crystal X-ray diffraction. The ruthenium atom in both molecules **1** and **2** adopts a *pseudo* octahedral configuration containing a cyclometalated ptpy ligand. The Ru–C(ptpy) and Ru–N bond lengths in **1** are 2.049(3) and 2.089(2) Å, respectively. The corresponding bond lengths for **2** are 2.025(9) and 2.089(7) Å.

**Key words:** Arene-Ruthenium, Ruthenacycle, Cyclometalated Ligands, Organometallic Compounds

## Introduction

The half-sandwich organoruthenium(II) complexes present a wide of potential applications in homogeneous catalysis for a variety of organic transformation reactions [1,2]. Accordingly, the coordination chemistry of such molecules is also interesting with respect to their reactivities [3]. Compared with most reports of organoruthenium complexes supported by neutral phosphane and polypyridyl ligands, relatively few ruthenium-ppy complexes (ppyH = 2-phenylpyridine) in which ppy is an anionic N,C-chelate ligand have been synthesized [4,5]. Examples of structurally characterized organoruthenium-ppy complexes include *trans*- $[\text{Ru}(\text{ppy})(\text{PPh}_3)_2(\text{CO})\text{Cl}]$  [6],  $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{ppy})\text{Cl}] \cdot \text{HgCl}_2$  [7] and  $[(\text{Cp}^*\text{Ru}(\text{ppy})(\text{NO}))][\text{OTf}]$  [8], of which it is interesting to note that the facile aromatic C–H bond activation in  $[(\text{Cp}^*\text{Ru}(\text{CH}_3)(\text{ppy})(\text{NO}))][\text{OTf}]$  gave stable high-valent ruthenium(IV) complexes [8]. The synthesis of ruthenium-ppy complexes is dependently dictated by intramolecular C–H activation of the phenyl ring in the *ortho* position. A typical method is the use of organomercurials because transmetalation reactions may easily result in the formation of cycloruthenated complexes in relatively high yields [9]. Recently, we have isolated new cyclometalated ruthenium com-

pounds containing C,N ligands by organomercurial transmetalation reactions [10]. In the course of our current research on ruthenium-ppy complexes, we herein report the syntheses of two organoruthenium complexes with cyclometalating 2-pyridyl-*m*-tolyl (ptpy) ligands and their characterization by spectroscopic data and single-crystal X-ray diffraction.

## Experimental Section

### Generals

All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were purified, distilled and degassed prior to use. NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300 MHz for <sup>1</sup>H (relative to SiMe<sub>4</sub>), and mass spectra were performed on a Finnigan TSQ 7000 spectrometer. Elemental analyses were performed by Medac Ltd., Surrey, UK.

$[(\eta^6\text{-arene})\text{RuCl}_2]_2$  (arene = C<sub>6</sub>Me<sub>6</sub> or *p*-cymene) [11] and  $[\text{Hg}(\text{ptpy})_2]$  [12] were synthesized according to literature methods.

### Syntheses

$[(\eta^6\text{-C}_6\text{Me}_6)\{(\text{ptpy})_2(\mu\text{-Hg}_2\text{Cl}_6)\}]$  (**1**)

A mixture of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}(\mu\text{-Cl})]_2$  (90 mg, 0.135 mmol) and  $[\text{Hg}(\text{ptpy})_2]$  (73 mg, 0.135 mmol) in THF (25 mL) was stirred at reflux for 6 h. The solvent was pumped off, and the residue was washed twice with Et<sub>2</sub>O and then

extracted with  $\text{CH}_2\text{Cl}_2$ . Recrystallization from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  gave the orange crystalline product. Yield: 113 mg, 78 %. –  $^1\text{H}$  NMR ( $[\text{D}_6]\text{acetone}$ ):  $\delta$  = 1.76 (s, 18H,  $\text{C}_6\text{Me}_6$ ), 2.56 (s, 3H,  $\text{CH}_3$ ), 7.34 (t,  $J$  = 7.8 Hz, 1H), 7.39 (d,  $J$  = 7.1 Hz, 1H), 7.74 (d,  $J$  = 6.8 Hz, 1H), 8.21 (dd,  $J$  = 8.2 Hz, 2H), 8.53 (d,  $J$  = 7.3 Hz, 1H), 9.04 (d,  $J$  = 6.4 Hz, 1H). – MS (FAB):  $m/z$  = 1477 ( $\text{M}^+$ ), 433 [ $(\text{C}_6\text{Me}_6)\text{Ru}(\text{ptpy}) + 1$ ] $^+$ . –  $\text{C}_{48}\text{H}_{56}\text{N}_2\text{Cl}_6\text{Hg}_2\text{Ru}_2$  (1476.97): calcd. C 39.0, H 3.79, N 1.90; found C 38.7, H 3.72, N 1.87.

$[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{ptpy})(\text{ClHgCl}_2)]$  (**2**)

This compound was prepared similarly as described for **1** using  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$  (90 mg, 147 mmol) instead of  $[(\eta^6\text{-}\text{C}_6\text{Me}_6)\text{RuCl}_2]_2$ . Recrystallization from  $\text{CH}_2\text{Cl}_2$ -hexane afforded orange crystals which were suitable for X-ray diffraction analysis. Yield: 72 mg, 64 %. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 0.95 (dd,  $J$  = 7.2 Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 1.25 (septet,  $J$  = 7.8 Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 2.12 (s, 3H,  $\text{CH}_3$ ), 2.42 (s, 3H,  $\text{CH}_3$ ), 5.08 and 5.25 (dd, each  $J$  = 6.2 Hz, 2H,  $\text{C}_6\text{H}_4$ ), 5.64 (d,  $J$  = 6.4 Hz, 2H,  $\text{C}_6\text{H}_4$ ), 6.90 (d,  $J$  = 7.4 Hz, 1H), 7.03 (t,  $J$  = 7.2 Hz, 1H), 7.06 (t,  $J$  = 7.4 Hz, 1H), 7.56 (d,  $J$  = 6.9 Hz, 1H), 7.68 (dd,  $J$  = 6.9 Hz, 2H), 8.08 (d,  $J$  = 7.0 Hz, 1H), 9.19 (d,  $J$  = 6.8 Hz, 1H). – MS (FAB):  $m/z$  = 709 [ $\text{M}-1$ ] $^+$ , 403 [ $(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{ptpy})$ ] $^+$ . –  $\text{C}_{22}\text{H}_{24}\text{NCl}_3\text{HgRu}$  (710.43): calcd. C 37.2, H 3.38, N 1.97; found C 37.9, H 3.32, N 1.96.

Crystal structure determination

An orange single crystal of **1** ( $0.40 \times 0.35 \times 0.10 \text{ mm}^3$ ) or **2** ( $0.26 \times 0.23 \times 0.18 \text{ mm}^3$ ) was mounted in random orientation on a glass fiber. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer with  $\text{MoK}\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 100 K using an  $\omega$  scan mode. The collected frames were processed with the software SAINT [13]. The data were corrected for absorption using the program SADABS [14]. Structures were solved by Direct Methods and refined by full-matrix least-squares on  $F^2$  using the SHELXTL software package [15]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically ( $\text{C}_{\text{sp}^3}\text{-H}$  = 0.96 and  $\text{C}_{\text{sp}^2}\text{-H}$  = 0.93 Å) and included in the structure factor calculations with assigned isotropic displacement parameters but were not refined. The largest peaks in the final difference maps with heights of 1.83 (for **1**) and 3.86  $\text{e Å}^{-3}$  (for **2**) are in the vicinity of the mercury atoms. The crystal data, data collection parameters and details of the structure refinement are given in Table 1.

Crystal data (excluding structure factors) have been deposited with The Cambridge Crystallographic Data Centre as supplementary publications CCDC 269636 and 269637. Copies of the data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Table 1. Crystal data, data collection parameters and details of the structure refinement.

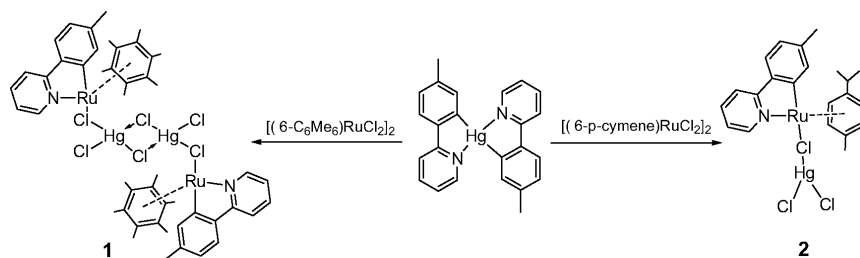
Complex	<b>1</b>	<b>2</b>
Empirical formula	$\text{C}_{48}\text{H}_{56}\text{N}_2\text{Cl}_6\text{Hg}_2\text{Ru}_2$	$\text{C}_{22}\text{H}_{24}\text{NCl}_3\text{HgRu}$
Formula weight	1476.97	710.43
Color, habit	orange, plate	orange, prism
Crystal size [ $\text{mm}^3$ ]	$0.40 \times 0.35 \times 0.10$	$0.26 \times 0.23 \times 0.18$
Crystal system	— triclinic —	
Space group	— $P\bar{1}$ —	
$a$ [Å]	10.3229(5)	10.278(4)
$b$ [Å]	10.8116(5)	10.433(4)
$c$ [Å]	11.1846(5)	11.401(4)
$\alpha$ [deg]	73.725(1)	86.401(6)
$\beta$ [deg]	84.613(1)	82.402(6)
$\gamma$ [deg]	84.668(1)	68.637(6)
Volume [ $\text{Å}^3$ ]	1190.2(1)	1128.4(7)
$Z$	1	2
Calcd. density [ $\text{g cm}^{-3}$ ]	2.06	2.09
Absorption coefficient [ $\text{mm}^{-1}$ ]	7.43	7.83
Temperature [K]	— 100(2) —	
$F(000)$ [e]	708	676
Radiation	— $\text{MoK}\alpha$ ( $\lambda$ = 0.71073 Å) —	
Reflections collected	13821	7270
Independence reflections	5573 ( $R_{\text{int}}$ = 0.026)	4985 ( $R_{\text{int}}$ = 0.067)
Refls. with $I \geq 2\sigma(I)$	5294	3357
Weighting scheme	*	$W = [\sigma^2(F_o^2)]$
Parameters refined	278	253
Final $R$ indices (all data)	$R1 = 0.026$ , $wR2 = 0.058$	$R1 = 0.075$ , $wR2 = 0.106$
Goodness of fit (GoF)	1.03	0.83
Final difference peaks [ $\text{e Å}^{-3}$ ]	+1.83, −0.75	+3.86, −2.20

$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ ;  $wR2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^2]^{1/2}$ ;  
GoF =  $[\Sigma w(|F_o| - |F_c|)^2/(N_{\text{obs}} - N_{\text{param}})]^{1/2}$ .

\*  $W = [\sigma^2(F_o^2) + 0.0316P^2 + 0.2129P]$  where  $P = (F_o^2 + 2F_c^2)/3$ .

## Results and Discussion

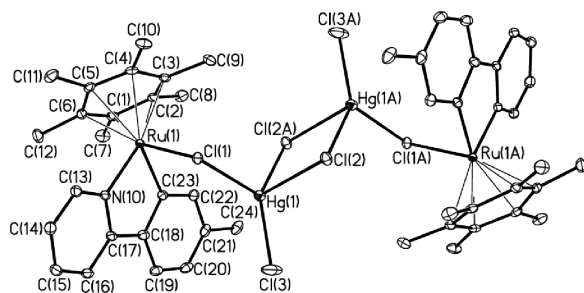
Transmetalation reaction of organomercurials with metal halide complexes may effectively give cyclometalated compounds in good yields. The driving force of the reaction stems mainly from the concurrent formation of insoluble mercuric chloride  $\text{HgCl}_2$  [16]. Moreover, the excess chloride ion enables the trapping of  $\text{HgCl}_2$  and the subsequent formation of  $\text{HgCl}_3^-$ , also formulated as  $\text{Hg}_2\text{Cl}_6^{2-}$  [17]. Thus, treatment of  $[\text{Hg}(\text{ptpy})_2]$  with the chloride-bridged dimeric complexes  $[(\text{arene})\text{RuCl}(\mu\text{-Cl})]_2$  (arene =  $\eta^6\text{-C}_6\text{Me}_6$  or  $\eta^6\text{-}p\text{-cymene}$ ) in THF solution at r.t. leads to cycloruthenation, resulting in the isolation of  $[(\eta^6\text{-}\text{C}_6\text{Me}_6)\text{Ru}(\text{ptpy})]_2(\mu\text{-Hg}_2\text{Cl}_6)$  **1** and  $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{ptpy})(\text{ClHgCl}_2)]$  **2** in 78 % and 72 % yields, respectively (Scheme 1). The  $\text{Hg}_2\text{Cl}_6^{2-}$  and  $\text{HgCl}_3^-$  anions formed in the reactions are coordinated to the  $[(\text{arene})\text{Ru}(\text{ptpy})]^+$  species to afford the neu-



Scheme 1.

Table 2. Selected bond lengths (Å) and bond angles (deg) for **1**.

Ru(1)–C(23)	2.049(3)	Ru(1)–N(10)	2.089(2)
Ru(1)–Cl(1)	2.4251(7)	Ru–C <sub>6</sub> Me <sub>6</sub> (centroid)	1.771(2)
Hg(1)–Cl(1)	2.5491(7)	Hg(1)–Cl(2)	2.9628(8)
Hg(1) <sup>#1</sup> –Cl(2)	2.4089(7)	Hg(1)–Cl(3)	2.3365(10)
C(23)–Ru(1)–N(10)	77.85(11)	C(23)–Ru(1)–Cl(1)	87.02(8)
N(10)–Ru(1)–Cl(1)	85.19(7)	Cl(3)–Hg(1)–Cl(2) <sup>#1</sup>	138.15(4)
Cl(3)–Hg(1)–Cl(1)	115.66(4)	Cl(2) <sup>#1</sup> –Hg(1)–Cl(1)	106.16(3)
Cl(3)–Hg(1)–Cl(2)	97.15(3)	Cl(2) <sup>#1</sup> –Hg(1)–Cl(2)	85.13(2)
Cl(1)–Hg(1)–Cl(2)	88.44(2)	Ru(1)–Cl(1)–Hg(1)	108.47(3)
Hg(1) <sup>#1</sup> –Cl(2)–Hg(1)	94.87(2)		

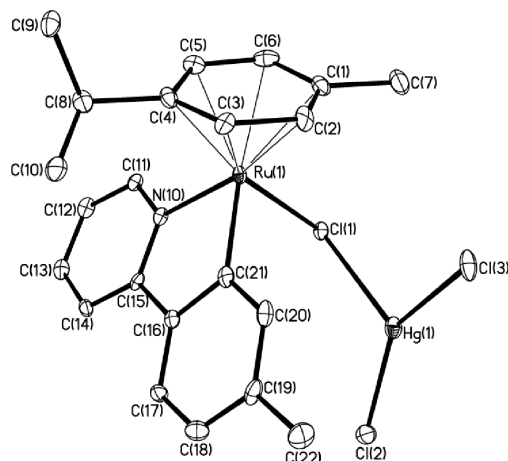
Symmetry code: <sup>#1</sup>  $-x+1, -y+1, -z+1$ .Fig. 1. Perspective view of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{ptpy})]_2 \cdot (\mu\text{-Hg}_2\text{Cl}_6)$  (**1**).

tral dimer **1** and monomer **2**, respectively. It should be noted that Djukic *et al.* previously reported that treatment of  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$  with  $\text{Hg}(\text{ppy})\text{Cl}$  afforded  $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{ppy})\text{Cl}] \cdot \text{HgCl}_2$  [7]. The  $^1\text{H}$  NMR spectra of **1** and **2** show four sets of doublet peaks in the range of  $\delta = 7.70\text{--}9.20$  ppm, assignable to four protons of the coordinating pyridine of the tpy ligands. The positive ion FAB mass spectra of **1** and **2** show  $[(\text{arene})\text{Ru}(\text{ptpy})]^+$  ions with the characteristic isotopic distribution patterns.

The structures of **1** and **2** were determined by single-crystal X-ray diffraction, and are shown in Figs. 1 and 2, respectively. Selected bond lengths and angles of **1** and **2** are given in Tables 2 and 3, respectively. Complex **1** is a dimer with the  $\text{Hg}_2\text{Cl}_6$  moiety as a bridging unit. This bridge is asymmetric with

Table 3. Selected bond lengths (Å) and bond angles (deg) for **2**.

Ru(1)–C(21)	2.025(9)	Ru(1)–N(10)	2.089(7)
Ru–cymene(centroid)	1.692(3)	Ru(1)–Cl(1)	2.425(2)
Hg(1)–Cl(2)	2.317(3)	Hg(1)–Cl(3)	2.369(2)
Hg(1)–Cl(1)	2.635(2)		
C(21)–Ru(1)–N(10)	78.3(3)	C(21)–Ru(1)–Cl(1)	85.3(2)
N(10)–Ru(1)–Cl(1)	87.49(17)	Cl(2)–Hg(1)–Cl(3)	144.93(9)
Cl(2)–Hg(1)–Cl(1)	108.89(8)	Cl(3)–Hg(1)–Cl(1)	106.18(8)
Ru(1)–Cl(1)–Hg(1)	105.03(7)		

Fig. 2. Perspective view of  $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{ptpy})\text{-(ClHgCl}_2)]$  (**2**).

short [2.4089(7) Å] and long [2.9628(8) Å] Hg–Cl bonds. Although complex **2** is a monomer with the unit  $\text{ClHgCl}_2$  in a  $\kappa^1$  mode, in the crystal two  $\text{HgCl}_3^-$  fragments interact weakly with “bridging” Hg–Cl distances of 3.034(2) Å, which are longer than that of dianionic  $\text{Hg}_2\text{Cl}_6^{2-}$  in **1**.

The ruthenium atoms in both complexes have a distorted octahedral configuration with a *p*-cymene or  $\text{C}_6\text{Me}_6$  ring at one face. The  $(\eta^6\text{-}p\text{-cymene})\text{Ru}$  and  $(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}$  fragments are coordinated by carbon and nitrogen atoms of a chelating tpy group and a chloride atom of a  $\text{Hg}_2\text{Cl}_6$  or  $\text{HgCl}_3$  moiety. The ruthenium atom in **1** is situated 1.771(2) Å above the cen-

ter of the phenyl contrail in the C<sub>6</sub>Me<sub>6</sub> moiety, while in **2** it is situated 1.692(3) Å above the *p*-cymene contrail. The Ru–C(pty) bond lengths in **1** and **2** are remarkably similar [2.049(3) and 2.025(9) Å, respectively], even though there are different arene ligands in the two complexes. The C–Ru–N angles in **1** [77.85(11)°] and **2** [78.3(3)°] agree well with those in [Cp\*Ru(ppy)(NO)]<sub>2</sub>[Hg<sub>2</sub>Cl<sub>6</sub>] [10] [77.95(17)°] and [(η<sup>6</sup>-*p*-cymene)Ru(ppy)Cl] · HgCl<sub>2</sub> [77.9(1)°] [7]. The Ru–Cl bond lengths of 2.4251(7) Å in **1** and 2.425(2) Å in **2** are normal. The mercury atom in **1** is in a highly distorted *pseudotetrahedral* configuration with a large range for the Cl–Hg–Cl angles from 85.13(2) to 138.15(4)°, together with four non-

equivalent Hg–Cl distances of 2.3365(10), 2.4089(7), 2.5491(7) and 2.9628(8) Å. The mercury atom in **2** lies in a distorted trigonal planar environment with three Hg–Cl distances of 2.317(3), 2.369(2) and 2.635(2) Å. The Ru–Cl–Hg bond angle in **2** [105.03(7)°] is 3.4° smaller than that in **1** [108.47(3)°].

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