

## Note

# Synthesis, structure and properties of cycloruthenated complexes: crystal structure of mono-chloro-( $\eta^6$ -*p*-cymene)-{(phenylazo)phenyl} ruthenium(II)

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Dedicated to Professor F. Albert Cotton on the occasion of his 70th birthday

**Abstract**

Two cycloruthenated complexes of formulation  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}(\text{L})]$ , where L = (phenylazo)phenyl (pap) (**1a**) and (4,4'-dimethyl)(phenylazo)phenyl (dmpap) (**1b**) were prepared from a transmetallation reaction involving  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$  and  $[\text{HgCl}(\text{L})]$  in refluxing  $\text{CHCl}_3$  or MeOH. The molecular structure of  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}(\text{pap})]$  (**1a**) has been determined by X-ray crystallography. The complex contains a  $\eta^6$ -*p*-cymene group, a chloride and a bidentate C,N-donor orthometallated (phenylazo)phenyl ligand. The complexes have been characterized from NMR data. The orthometallated carbon appears near  $\delta$  188 ppm in the  $^{13}\text{C}$ -NMR in  $\text{CDCl}_3$ . © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Arene-ruthenium; *ortho*-Metallation; Crystal structure; Azobenzene

**1. Introduction**

The half-sandwich ( $\eta^6$ -arene)ruthenium(II) complexes have drawn considerable current attention in asymmetric transformation reactions and in the development of the chemistry of optically active enantioselective catalytic systems [1–10]. The ancillary ligand bonded to ruthenium plays a vital role in such catalytic reactions. Earlier studies have shown that N,N- and N,O-donor bidentate ligands are useful in the synthesis of optically active diastereomeric complexes as well as for asymmetric induction studies [11–15]. The chemistry of cycloruthenated (arene)ruthenium(II) complexes are relatively scarce and only a few systems having C,N-donor bidentate ligands have been explored in diastereomeric reactions [3–6,14].

The present work stems from our interest to develop the chemistry of ( $\eta^6$ -arene)ruthenium complexes having C,N-donor azobenzene and related ligand systems.

Herein we report the synthesis, structure and properties of  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}(\text{L})]$ , where L is bidentate chelating C,N-donor (phenylazo)phenyl (**1a**) or (4,4'-dimethyl)(phenylazo)phenyl (**1b**) ligand. Complex **1a** has been structurally characterized.

**2. Results and discussion**

The complexes of formulation  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}(\text{L})]$  are prepared from a facile transmetallation reaction involving  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$  and the orthometallated mercury(II) complex  $\text{HgCl}(\text{L})$  in chloroform or methanol [L, (phenylazo)phenyl, **1a** or (4,4'-dimethyl)-(phenylazo)phenyl, **1b**]. The complexes are fairly air stable in the solid state but are unstable in the solution phase. Both the complexes are characterized from elemental analysis and NMR spectral data. The electronic spectra of the complexes show intense charge transfer bands involving the azofunctionality and *p*-cymene ligand near 450 nm in acetonitrile along with a very strong band near 330 nm. A relatively weak visible

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band is observed in the range 575–597 nm. The complexes are redox active and show an irreversible azo bond reduction at  $-1.15$  V and an irreversible oxidation process at  $0.9$  V vs. SCE in MeCN– $0.1$  M TBAP.

The  $^1\text{H-NMR}$  data suggest a 1:1 ratio of the *p*-cymene and the azophenyl ligands in **1a** and **1b**. The arene ligand displays a singlet for the methyl, two doublets and a septet for the  $\text{CHMe}_2$  in the range  $\delta$  0–3 ppm. The arene ring protons appear within  $\delta$  5–7 ppm. The appearance of two doublets for the two methyls of the  $\text{CHMe}_2$  moiety could be due to the diastereotropic nature of the methyl groups. The spectral features in the range  $\delta$  7–9 ppm are due to the chelating (phenylazo)phenyl ligand. The orthometalated phenyl group in **1b** shows a singlet at 8.22 ppm. The four doublets in the ranges 7.0–7.3 and 8.0–8.1 ppm are assignable to the aryl group protons of the bidentate ligand. The methyl groups of the ligand appear as two singlets near  $\delta$  2.5 ppm. The  $^{13}\text{C-NMR}$

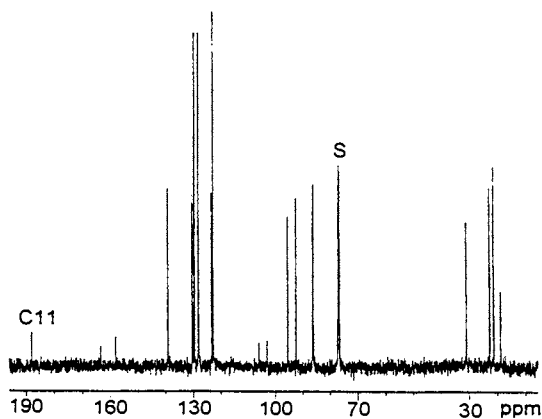


Fig. 1.  $^{13}\text{C-NMR}$  spectrum of **1a** in  $\text{CDCl}_3$  (S, solvent peak).

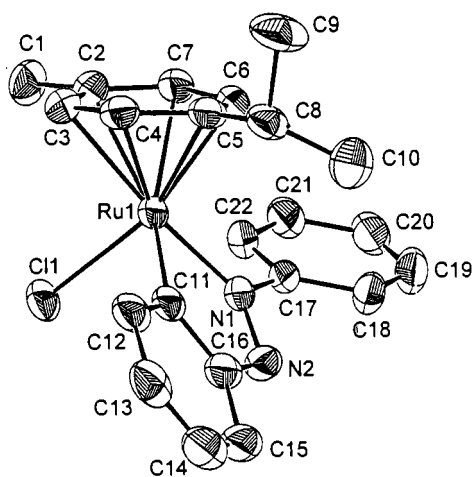


Fig. 2. ORTEP drawing giving 50% probability thermal ellipsoids and the atom labeling scheme of  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}(\text{pap})]$  (**1a**).

Table 1

Bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) for **1a** with estimated S.D.s in parentheses ( $\text{C}^\circ$ , the centroid of the  $\eta^6\text{-arene}$  ring)

Bond lengths			
Ru1–C2	2.344(4)	Ru1–C11	2.393(1)
Ru1–C3	2.217(4)	Ru1–C11	2.005(4)
Ru1–C4	2.193(5)	Ru1–N1	2.041(4)
Ru1–C5	2.169(4)	C5–C8	1.508(6)
Ru1–C6	2.154(5)	C8–C9	1.523(6)
Ru1–C7	2.321(4)	C8–C10	1.524(7)
C2–C3	1.429(6)	C1–C2	1.503(6)
C3–C4	1.383(6)	C2–C7	1.379(6)
C4–C5	1.427(6)	N1–C17	1.435(6)
C5–C6	1.411(7)	N1–N2	1.279(5)
C6–C7	1.421(6)	N2–C16	1.380(6)
C11–C12	1.397(7)	C11–C16	1.400(7)
C12–C13	1.389(7)	C14–C15	1.365(9)
C13–C14	1.377(8)	C15–C16	1.400(7)
Ru1– $\text{C}^\circ$	1.735(2)		
Bond angles			
C11–Ru1–N1	89.4(1)	C11–Ru1–C11	86.6(1)
C11–Ru1– $\text{C}^\circ$	125.2(4)	N1–Ru1–C11	75.8(2)
N1–Ru1– $\text{C}^\circ$	132.2(3)	C11–Ru1– $\text{C}^\circ$	130.8(6)
Ru1–N1–C17	124.0(3)	Ru1–N1–N2	121.4(4)
N1–N2–C16	111.1(4)	Ru1–C11–C16	114.2(4)
C11–C16–N2	117.4(4)	N2–C16–C15	119.2(6)
C14–C15–C16	118.6(6)	C13–C14–C15	119.9(6)
C12–C13–C14	121.3(6)	C11–C12–C13	121.1(5)
N1–C17–C18	120.5(5)	N1–C17–C22	119.1(4)
C5–C8–C9	108.7(4)	C5–C8–C10	114.0(5)
C9–C8–C10	111.4(5)	C1–C2–C3	120.7(4)
C2–C3–C4	122.0(4)	C1–C2–C7	121.6(5)
C3–C4–C5	121.0(5)	C4–C5–C6	116.1(4)
C5–C6–C7	122.3(4)	C4–C5–C8	120.5(5)
C6–C5–C8	123.4(4)		

spectra of the complexes show the M–C  $\sigma$ -bond formation. This characteristic signal is observed at  $\delta$  188.0 ppm for **1a** (Fig. 1) and  $\delta$  188.7 ppm for **1b**. The  $^{13}\text{C-NMR}$  spectral features of **1a** and **1b** are essentially same. The NMR data are consistent with those reported for related pap and 4,4'-dmpap complexes [15,16]. The assignments of the protons in **1a** have been made unambiguously from the 2D-NMR correlation spectra in  $\text{CDCl}_3\text{-TMS}$  and the crystal-structure data.

The complex  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}(\text{pap})]$  (**1a**) has been structurally characterized by X-ray crystallography. An ORTEP [17] view of the complex is shown in Fig. 2. Selected bond distances and bond angles are given in Table 1. The coordination geometry of the metal center is essentially octahedral with the  $\eta^6\text{-}p\text{-cymene}$  ring carbons occupying one face of the octahedron. The remaining sites are occupied by a chloride and a bidentate chelating C,N-donor (phenylazo)phenyl ligand. The Ru–C (arene) distances vary considerably from 2.154 to 2.334  $\text{\AA}$  [18,19]. The Ru(1)–C(11) bond of 2.005(4)  $\text{\AA}$  is marginally shorter than the similar Ru–C  $\sigma$ -bond distances reported in related  $(\eta^6\text{-}p\text{-cymene})$ ruthenium complexes [4].

In summary, we have synthesized new (arene)-ruthenium(II) complexes having C,N-donor bidentate (phenylazo)phenyl and (4,4'-dimethyl)(phenylazo)-phenyl ligands. The complexes with a labile binding site are suitable for stereochemical investigations in chloride substitution reactions and for reactions directed to the Ru–C  $\sigma$ -bond.

### 3. Experimental

All reactions were carried out in dry solvent under a dinitrogen atmosphere. Azobenzene, azotoluene and their mercury compounds were synthesized following literature procedures [20,21]. The precursor complex  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$  was made by a reported method [22]. All chemicals were of reagent grade and used as such.

Elemental analysis was performed on a Perkin–Elmer 2400 CHN analyzer. The  $^1\text{H}$ - and  $^{13}\text{C}$ - $\{^1\text{H}\}$ -NMR spectra were recorded on Bruker 200 MHz and Bruker DRX 400 (carbon channel 100.6 MHz) spectrometers, respectively. Tetramethylsilane (TMS) was used as a standard ( $\delta$  0.0 ppm). Electronic spectra were recorded on a Hitachi U-3400 spectrophotometer. Cyclic voltammetric measurements were performed using a PAR model 253 Versastat potentiostat/galvanostat with EG&G electrochemical software operating on WINDOWS 95. In the three-electrode configuration, a platinum button, a platinum wire, and a saturated calomel electrode (SCE) were used as working, auxiliary and reference electrodes, respectively. In the measurements, 0.1 M  $(\text{Bu}_4\text{N})\text{ClO}_4$  (TBAP) in acetonitrile solvent was used as a supporting electrolyte. The measurements were made at 25°C and the data were uncorrected for junction potentials. Ferrocene was used as standard to verify the potential observed against the SCE. The  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$  couple of ferrocene was observed at 0.43 V (versus SCE).

#### 3.1. Synthesis of $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}(\text{pap})]$ (**1a**)

A mixture of 0.3 g (0.49 mmol) of  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$  and 0.42 g (1.01 mmol) of  $\text{ClHg}(\text{pap})$  in 30 ml of  $\text{CHCl}_3$  was stirred for 48 h under refluxing condition. The resulting dark red solution was filtered, reduced to a volume of 5 ml and chromatographed on a neutral alumina column in  $\text{CHCl}_3$ . The major light green band was collected using  $\text{CHCl}_3$  as an eluant and a solid was obtained on evaporation of the solvent. The complex was subsequently crystallized from an acetone–toluene (1:1, v/v) mixture giving 0.27 g of the product as dark orange crystals. Anal. Found: C, 58.28; H, 5.10; N, 6.50;  $\text{C}_{22}\text{H}_{23}\text{N}_2\text{ClRu}$  requires: C, 58.47; H, 5.10; N, 6.20%. UV–vis data in MeCN

$[\lambda_{\text{max}}, \text{nm} (\epsilon, 1 \text{ mol}^{-1} \text{ cm}^{-1})]$ : 597 (525), 455 (3350), 332 (11400), 270 (10410).  $^1\text{H}$ -NMR [ $\text{CDCl}_3$ , 200 MHz,  $\delta$  in ppm,  $J$  in Hz]: 8.29 (1H, m,  $\text{H}_{12}$ ), 8.18 (3H, m,  $\text{H}_{15,18,22}$ ), 7.50 (3H, m,  $\text{H}_{19-21}$ ), 7.18 (2H, m,  $\text{H}_{13,14}$ ), 5.69 (1H, d,  $^3J_{\text{HH}} = 6.5$ ,  $\text{H}_4$ ), 5.54 (1H, d,  $^3J_{\text{HH}} = 6.1$ ,  $\text{H}_7$ ), 5.16 (1H, d,  $^3J_{\text{HH}} = 6.5$ ,  $\text{H}_3$ ), 5.06 (1H, d,  $^3J_{\text{HH}} = 6.0$ ,  $\text{H}_6$ ), 2.27 (1H, sp,  $^3J_{\text{HH}} = 7.0$ ,  $\text{H}_8$ ), 2.11 (3H, s,  $\text{H}_{1A-C}$ ), 0.90 (3H, d,  $^3J_{\text{HH}} = 7.0$ ,  $\text{H}_{9A-C}$ ), 0.73 (3H, d,  $^3J_{\text{HH}} = 7.0$ ,  $\text{H}_{10A-C}$ ) (s, singlet; d, doublet; sp, septet; m, complex multiplet pattern). The hydrogen atom numbering scheme is same as the carbon atom labeling scheme shown in Fig. 2.  $^{13}\text{C}$ -NMR [ $\text{CDCl}_3$ , 100.61 MHz;  $\delta$ , ppm]: 188.05 ( $\text{C}_{11}$ ), 163.58, 158.16 ( $\text{C}_{16,17}$ ), 139.23, 130.52, 129.72, 128.23, 123.56, 122.98 ( $\text{C}_{12-15}$ ,  $\text{C}_{18-22}$ ), 106.14, 103.19, 95.58, 92.52, 86.43, 86.13 ( $\text{C}_{2-7}$ ), 30.79 ( $\text{C}_1$ ), 22.64, 21.19 ( $\text{C}_{9,10}$ ), 18.79 ( $\text{C}_8$ ).

#### 3.2. Synthesis of $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}(4,4'\text{-dmpap})]$

A mixture of 0.3 g (0.49 mmol) of  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$  and 0.45 g (1.01 mmol) of  $\text{ClHg}(\text{dmpap})$  was stirred for 28 h in refluxing methanol. The resulting solution was filtered through Celite and the solvent was evaporated to isolate the solid, which was then dissolved in 5 ml of  $\text{CHCl}_3$ . Addition of cold *n*-hexane gave a crystalline solid of **1b** (0.4 g). The solid was washed with cold hexane and dried in vacuum. Anal. Found: C, 60.20; H, 5.41; N, 5.92.  $\text{C}_{24}\text{H}_{27}\text{N}_2\text{ClRu}$  requires: C, 60.06; H, 5.63; N, 5.84%. UV–vis data in MeCN  $[\lambda_{\text{max}}, \text{nm} (\epsilon, 1 \text{ mol}^{-1} \text{ cm}^{-1})]$ : 577 (564), 451 (2160), 340 (13800).  $^1\text{H}$ -NMR [ $\text{CDCl}_3$ , 200 MHz,  $\delta$  in ppm,  $J$  in Hz]: 8.23 (1H, s,  $\text{H}_{12}$ ), 8.11 (1H, d,  $^3J_{\text{HH}} = 8.0$ ,  $\text{H}_{15}$ ), 8.02 (2H, d,  $^3J_{\text{HH}} = 8.0$ ,  $\text{H}_{18,22}$ ), 7.29 (2H, d,  $^3J_{\text{HH}} = 8.0$ ,  $\text{H}_{19,21}$ ), 7.06 (1H, d,  $^3J_{\text{HH}} = 8.0$ ,  $\text{H}_{14}$ ), 5.69, 5.64, 5.29, 5.10 (4H, 4d,  $^3J_{\text{HH}} = 6.0$ ,  $\text{H}_{3,4,6,7}$ ), 2.50 (3H, s,  $\text{Me}-\text{C}_{13}$ ), 2.47 (3H, s,  $\text{Me}-\text{C}_{20}$ ), 2.23 (1H, sp,  $\text{H}_8$ ), 2.15 (3H, s,  $\text{H}_{1A-C}$ ), 0.86, 0.72 ( $2 \times 3\text{H}$ , 2d,  $^3J_{\text{HH}} = 6.8$ ,  $\text{H}_{9A-C}$ ,  $\text{H}_{10A-C}$ ).  $^{13}\text{C}$ -NMR [ $\text{CDCl}_3$ , 100.61 MHz;  $\delta$ , ppm] 188.68 ( $\text{C}_{11}$ ), 162.50, 156.68 ( $\text{C}_{16,17}$ ), 141.06, 140.50, 130.70, 129.48, 126.12, 125.70, 123.63 ( $\text{C}_{12-15}$ ,  $\text{C}_{18-22}$ ), 106.41, 103.27, 96.21, 92.68, 87.24, 86.68 ( $\text{C}_{2-7}$ ), 31.52, 31.00 ( $\text{C}_1$ ,  $\text{C}_{\text{H}_3-\text{C}_{13}}$ ), 23.33, 22.90, 21.91 ( $\text{C}_{9,10}$ ,  $\text{C}_{\text{H}_3-\text{C}_{20}}$ ), 19.54 ( $\text{C}_8$ ).

#### 3.3. X-ray structure determination of **1a**

Orange needles of **1a** were obtained by cooling a solution of the complex in acetone–toluene mixture (1:1, v/v) at  $-5^\circ\text{C}$ . Unit cell dimensions were obtained on an Enraf–Nonius CAD4 diffractometer equipped with graphite monochromated Mo– $\text{K}_\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) using a crystal of approximate dimension  $0.32 \times 0.13 \times 0.49 \text{ mm}^3$ . Intensities of reflections ( $-10 \leq h \leq 10$ ;  $0 \leq k \leq 18$ ;  $0 \leq l \leq 17$ ) within the range  $4^\circ \leq 2\theta \leq 51^\circ$  were measured in a  $\omega/2\theta$  scan

mode. Out of 3537 unique reflections, 2571 data with  $I \geq 2\sigma(I)$  were used for the refinement of the structure. The intensity data were corrected for Lorentz and polarization effects. Crystal data:  $C_{22}H_{23}N_2ClRu$ ,  $M_r = 451.94$ , monoclinic,  $P2_1/a$ ,  $a = 8.806(3)$ ,  $b = 15.881(2)$ ,  $c = 14.758(2)$  Å,  $\beta = 103.61(3)^\circ$ ,  $U = 2006.1(9)$  Å<sup>3</sup>,  $D_{\text{calc}} = 1.496$  g cm<sup>-3</sup>,  $Z = 4$ ,  $F(000) = 920$ ,  $\mu(\text{Mo-K}\alpha) = 9.22$  cm<sup>-1</sup>,  $T = 293(2)$  K.

The structure was solved by Patterson's heavy atom method, which revealed the position of the ruthenium atom in the crystallographic asymmetric unit. The remaining atoms were located in successive difference Fourier maps. Refinements of the structure were made by full-matrix least-squares procedure based on  $F^2$ . An empirical absorption correction [23] on the data was made after obtaining the complete structural model. The transmission coefficients were in the range 0.73–1.0. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to the atoms in the complex were generated and assigned isotropic thermal parameters, riding on their parent atoms and used for structure factor ( $F^2$ ) calculation only. The refinement converged to  $R_1 = 0.0361$  and  $wR_2 = \{\Sigma w[(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]\}^{1/2} = 0.0684$  with the weighting scheme  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$  where  $P = (F_o^2 + 2F_c^2)/3$ ,  $a = 0.0233$  and  $b = 2.13$  using 235 parameters for 2571 reflections [ $R$  indices (all data):  $R = 0.0657$ ,  $wR = 0.0818$ ]. The final difference Fourier map showed the largest peak and hole as 0.35 and  $-0.48$  e Å<sup>-3</sup>. The goodness-of-fit on  $F^2$  was 1.121. All calculations were carried out using SHELXS-86 and SHELXL-93 programs [24].

#### 4. Supplementary material

Crystallographic data (atomic coordinates, bond lengths, bond angles and thermal parameters) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 134995. 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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