

# Synthesis and characterization of areneruthenium(II) dialkyldithiophosphate complexes: single crystal structure of $[\text{Ru}\{\text{SSP}(\text{OEt})_2\}(\eta^6\text{-p-cymene})(\text{PPh}_3)][\text{BPh}_4]$

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## Abstract

Reactions of  $[\text{RuCl}_2(\eta^6\text{-arene})_2]$  with ammonium salt of dialkyldithiophosphoric acid in 1:1 and 1:2 stoichiometry readily gave complexes of the type  $[\text{Ru}\{\text{SSP}(\text{OR})_2\}(\text{Cl})(\eta^6\text{-arene})]$  (arene = benzene, p-cymene; R = Et, <sup>n</sup>Pr, <sup>i</sup>Pr, <sup>n</sup>Bu or <sup>s</sup>Bu) and  $[\text{Ru}\{\text{SSP}(\text{OR})_2\}_2(\eta^6\text{-arene})]$  (R = Et; arene = p-cymene). The former complexes, on treatment with  $\text{NaBPh}_4$  in acetone followed by addition of a neutral donor ligand (L), afforded cationic complexes  $[\text{Ru}\{\text{SSP}(\text{OEt})_2\}(\eta^6\text{-p-cymene})\text{L}][\text{BPh}_4]$  (L = py,  $\text{PPh}_3$ ,  $(\text{p-FC}_6\text{H}_4)_3\text{P}$ ,  $\text{AsPh}_3$ ). All the complexes were characterized by elemental analysis and NMR (<sup>1</sup>H, <sup>31</sup>P) data. A single crystal X-ray structure determination of  $[\text{Ru}\{\text{SSP}(\text{OEt})_2\}(\eta^6\text{-p-cymene})(\text{PPh}_3)][\text{BPh}_4]$  has established an octahedral configuration around the ruthenium atom. The structure consists of a ruthenium centre bonded to an  $\eta^6\text{-p-cymene}$ , a chelated dithiophosphate and a unidentate triphenylphosphine ligand.

**Keywords:** Ruthenium; Arene–ruthenium; Dialkyldithiophosphate; Crystal structure

## 1. Introduction

Transition metal complexes with sulphur ligands are of significance because of diverse bonding possibilities and their role in homogeneous catalysis. Although a number of organometallic [1] and classical coordination [2] complexes of ruthenium with thiolate and dithio acids ( $\text{R}_2\text{NCS}_2^-$ ,  $\text{ROCS}_2^-$ ,  $\text{RCS}_2^-$ ,  $\text{R}_2\text{PS}_2^-$ ,  $(\text{RO})_2\text{PS}_2^-$ ) have been studied over the last two decades or so, there has been an increased interest in such complexes due to high catalytic activity of  $\text{RuS}_2$  in various hydrotreating processes [3]. Numerous organoruthenium complexes based on 'CpRu' [1,4,5] 'Ru(CO)' [1,6], 'Ru(CO)H' [7] and 'Ru(diene)' [8] have been studied in considerable detail. The arene–ruthenium complexes such as  $[\text{RuCl}_2(\text{arene})_2]$  and  $[\text{RuCl}_2(\text{PR}_3)(\text{arene})]$  have been used as homogeneous catalysts [9,10]. However, there is a paucity of data on arene–ruthenium complexes containing sulphur ligands [11,12]. This may be due in part to easy elimination of arene ligands from the com-

plexes. Thus, attempts to isolate complexes of the type  $[\text{Ru}(\text{S-S})_2(\eta^6\text{-arene})]$  ( $\text{S-S} = \text{ROCS}_2^-$  or  $\text{R}_2\text{NCS}_2^-$ ) were unsuccessful, whereas complexes with thiophosphinic acids ( $\text{S-S} = \text{SSPR}_2$ ) lost arene slowly [11]. We have synthesised a series of arene–ruthenium complexes with dithiophosphoric acids, and have established the structure of at least one complex by X-ray diffraction. The results of this work are reported herein.

## 2. Results and discussion

Reactions of  $[\text{RuCl}_2(\eta^6\text{-arene})_2]$  with ammonium salt of dialkyldithiophosphoric acid in 1:1 and 1:2 stoichiometry readily gave arene–ruthenium(II) dialkyldithiophosphate complexes of the type  $[\text{Ru}\{\text{SSP}(\text{OR})_2\}(\text{Cl})(\eta^6\text{-arene})]$  (**1**) [arene, R = benzene, Et (**1a**); benzene, <sup>i</sup>Pr (**1b**); p-cymene, Et (**1c**); p-cymene, <sup>n</sup>Pr (**1d**); p-cymene, <sup>i</sup>Pr (**1e**); p-cymene, <sup>n</sup>Bu (**1f**); p-cymene, <sup>s</sup>Bu (**1g**)] and  $[\text{Ru}\{\text{SSP}(\text{OR})_2\}_2(\eta^6\text{-arene})]$  (**2**) (arene = p-cymene; R = Et) respectively. The complex  $[\text{Ru}\{\text{SSP}(\text{OEt})_2\}(\text{Cl})(\eta^6\text{-p-cymene})]$  on treatment with  $\text{NaBPh}_4$

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followed by addition of a neutral donor ligand in acetone, yielded  $[\text{Ru}(\text{SSP}(\text{OEt})_2)(\text{L})(\eta^6\text{-p-cymene})][\text{BPh}_4]$  (**3**) [ $\text{L} = \text{py}$  (**3a**),  $\text{PPh}_3$  (**3b**),  $(\text{p-FC}_6\text{H}_4)_3\text{P}$  (**3c**),  $\text{AsPh}_3$  (**3d**)].

The  $^{31}\text{P}$  NMR spectra of **1** displayed a single resonance for the dithiophosphate ligand. The  $[\text{RuH}(\text{CO})\{\text{SSP}(\text{O}^t\text{Bu})_2\}(\text{PPh}_3)_2]$  and organoplatinum complexes containing  $(^t\text{BuO})_2\text{PSS}$  ligand exhibit separate resonances for *meso*, *RR* and *SS* forms [7a,13], with peak separation of 0.1 to 0.4 ppm. However, in the case of **1g** only one single resonance was observed, possibly the separation for different forms is of the order of digital resolution. The complex **2** showed two singlets at 113.6 and 98.1 ppm. The  $^{31}\text{P}$  NMR spectra of **3** containing phosphine ligands exhibited two doublets attributable to the dithiophosphate and phosphine ligands. The magnitude of  $^3J(\text{P-P})$  (22 Hz) is in agreement with those reported for organometallic Ru, Pd and Pt dithiophosphate complexes [4,13,14].

The  $^1\text{H}$  NMR spectra of **1–3** showed expected integration and peak multiplicities. The spectra displayed a single set of resonances for arene protons. The alkoxy groups of the dithio ligand in **1** and **2** showed two separate sets of resonances, indicating non-equivalence of OR groups. One set of resonances (the downfield signals) are little affected on changing the chloride group in **1** with a neutral donor ligand in **3**. However, the second set of proton resonances showed ligand dependence, and shielded further on changing chloride (**1**) and L (**3**). This may be attributed to the chemical shift anisotropy due to aromatic rings. It is evident from the structure of **3b** that one of the OEt groups lies down the arene ring and one of the phenyl rings of the  $\text{PPh}_3$  ligand is parallel to this group, whereas the second OEt group lies outside the ring currents and hence is little influenced by the ligand variations. The  $^1\text{H}$  NMR spectrum of **2** showed three sets of dithio ligand proton resonances, assignable to a bidentate and a monodentate ligand moieties. For the monodentate dithio ligand only one set of resonances was observed.

The structure of  $[\text{Ru}(\text{SSP}(\text{OEt})_2)(\eta^6\text{-p-cymene})(\text{PPh}_3)]^+[\text{BPh}_4]^-$  (**3b**) was established by single crystal X-diffraction analysis. The molecular structure of the cation is shown in Fig. 1. The atomic coordinates and selected bond lengths and angles are given in Tables 1 and 2 respectively.

The ruthenium atom in the molecule adopts an octahedral configuration, having a p-cymene ligand at one face. The Ru atom is situated 1.746(2) Å above the centre of the planar p-cymene ring. The dithiophosphate ligand is symmetrically chelated to the ruthenium atom, the two Ru–S distances are essentially the same, i.e. 2.431 Å, and are in good agreement with the values reported recently for the thiolate-bridged complex  $[\{\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)_2(\mu\text{-SPh})_3\}\text{Cl} \cdot 2\text{CHCl}_3]$  [12]. The Ru–C bond distances are in the range 2.204(4)–2.261(5)

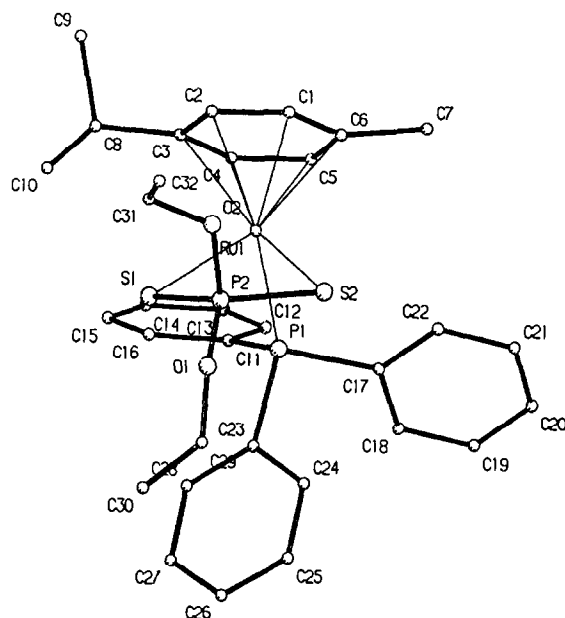


Fig. 1. Molecular structure of  $[\text{Ru}(\text{SSP}(\text{OEt})_2)(\eta^6\text{-p-cymene})(\text{PPh}_3)]^+$  with the crystallographic numbering scheme for non-hydrogen atoms.

Å (mean 2.257 Å), slightly longer than those reported in  $[\text{RuCl}_2(\eta^6\text{-p-cymene})(\text{PH}_2\text{Cy})]$  [15],  $[\text{RuCl}(\eta^6\text{-p-cymene})\{\text{C}_6\text{H}_4\text{CH}=\text{NCH}(\text{Me})\text{Ph}\}]$  [16] and  $[\text{RuCl}(\mu\text{-N}_3)(\eta^6\text{-p-cymene})_2]$  [17]. The Ru–P distance (2.3558 Å) is slightly longer than that reported in  $[\text{RuCl}_2(\eta^6\text{-p-cymene})(\text{PH}_2\text{Cy})]$  (2.299 Å) [15]. The P–S bond lengths of 1.989(2) and 1.971(2) Å are intermediate between double bond (1.94 Å) and single bond (2.09 Å) values, confirming the partial double bond character. The four-membered chelate ring  $\text{RuS}_2\text{P}$  is planar [the phosphorus atom shows maximum deviation 0.228(1) Å from the plane formed by Ru, S(1), S(2), P(2) atoms]. In metal complexes the four-membered ‘ $\text{MS}_2\text{P}$ ’ ring has been shown to adopt either a planar [14,18] or a non-planar [19,20] conformation. The anion  $[\text{BPh}_4]^-$  has the usual tetrahedral geometry. The bond lengths and angles are similar to those reported previously for this anion [21,22].

### 3. Experimental details

The complexes  $[\text{RuCl}_2(\eta^6\text{-benzene})_2]$ ,  $[\text{RuCl}_2(\eta^6\text{-p-cymene})_2]$  [23] and the ammonium salt of the dialkyldithiophosphoric acids [24] were prepared by published methods. All the preparations were carried out under nitrogen atmosphere. Elemental analysis for C, H, N were carried out in the Analytical Chemistry Division of this Research Centre.  $^1\text{H}$  and  $^{31}\text{P}\{\text{H}\}$  NMR spectra were recorded in  $\text{CDCl}_3$  on a Varian XLR-300 instrument operating at 300 and 121.421 MHz respectively. Chemical shifts are relative to internal solvent peak

(CHCl<sub>3</sub>,  $\delta$  7.26 ppm for <sup>1</sup>H) and external 85% H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P.

### 3.1. Preparation of [Ru{SSP(OEt)<sub>2</sub>}(Cl)( $\eta^6$ -*p*-cymene)] (1c)

To an ethanol (5 ml) solution of NH<sub>4</sub>SSP(OEt)<sub>2</sub> (116 mg, 0.57 mmol), was added a mixture of dichloromethane and diethylether (1 : 1 v/v, 20 ml). To this solution was added solid [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (169 mg, 0.28 mmol), and the whole was stirred at room temperature for 3 h during which time a wine red solution was obtained. The solvents were evaporated in vacuo, leaving a brown paste. This was treated with diethylether and water. The organic layer was separated, washed with water, dried over CaCl<sub>2</sub> and filtered. The filtrate was concentrated in vacuo. The brown residue was dissolved in a minimum added quantity of diethylether and hexane (10 ml), which on cooling in a freezer for 24 h gave brown–red crystals (187 mg, 74%). M.p. 75–76°C. Anal. Found: C, 37.3; H, 5.1. C<sub>14</sub>H<sub>24</sub>O<sub>2</sub>PS<sub>2</sub>ClRu Calc.: C, 36.9; H, 5.4%. <sup>1</sup>H NMR  $\delta$ : 1.33 (d, 7 Hz, CHMe<sub>2</sub>), 2.25 (s, Me); 2.95 (septet, 7 Hz, CH <); 5.25 (d), 5.49 (d) (each 6 Hz, C<sub>6</sub>H<sub>4</sub>) [arene protons]; 1.22 (t), 1.38 (t) (each 7 Hz, OC–CH<sub>3</sub>); 4.09 (m, OCH<sub>2</sub>–) [dithiophosphate ligand protons]. <sup>31</sup>P NMR  $\delta$ : 103.3 ppm. Mass spectrum of the sample showed a molecular ion peak at 456.

All other complexes were prepared similarly, except in place of ethanol an alcohol corresponding to the alkoxy group on phosphorus was used. Pertinent data for these complexes are given as follows.

[RuCl{SSP(OEt)<sub>2</sub>}( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)] (1a). M.p. 145–150°C (decomp.). <sup>1</sup>H NMR  $\delta$ : 5.68 (s, C<sub>6</sub>H<sub>6</sub>); 1.24 (t), 1.40 (t) (each 7 Hz, OCCCH<sub>3</sub>); 4.10 (m, OCH<sub>2</sub>). <sup>31</sup>P NMR  $\delta$ : 103.5. Although samples were spectroscopically pure, microanalyses were not reproducible.

[RuCl{SSP(O<sup>*i*</sup>Pr)<sub>2</sub>}( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)] (1b). M.p. 115–116°C. <sup>1</sup>H NMR  $\delta$ : 5.65 (s, C<sub>6</sub>H<sub>6</sub>); 1.21 (d), 1.38 (d) (each 6.2 Hz, OCHMe<sub>2</sub>); 4.63 (m), 4.89 (m) (OCH <). <sup>31</sup>P NMR  $\delta$ : 100.6. Although samples were spectroscopically pure, microanalyses were not reproducible.

[RuCl{SSP(O<sup>*n*</sup>Pr)<sub>2</sub>}( $\eta^6$ -*p*-cymene)] (1d). Recrystallized from diethylether–hexane in 43% yield. M.p. 55°C. Anal. Found: C, 39.2; H, 5.9. C<sub>16</sub>H<sub>28</sub>O<sub>2</sub>PS<sub>2</sub>ClRu Calc.: C, 39.7; H, 5.8%. <sup>1</sup>H NMR  $\delta$ : 1.33 (d, 7 Hz, CHMe<sub>2</sub>); 2.25 (s, Me), 2.96 (septet, 7 Hz, CH <); 5.25 (d), 5.49 (d) (each 6 Hz, C<sub>6</sub>H<sub>4</sub>) [arene protons]; 0.87 (t), 0.99 (t) (each 7 Hz, OCCMe); 1.60 (septet), 1.75 (septet) (each 7 Hz, OCCCH<sub>2</sub>–); 3.98 (m, OCH<sub>2</sub>); [dithiophosphate]. <sup>31</sup>P NMR  $\delta$ : 103.2.

[RuCl{SSP(O<sup>*i*</sup>Pr)<sub>2</sub>}( $\eta^6$ -*p*-cymene)] (1e). Recrystallized from dichloromethane–diethylether–hexane mixture in 40% yield. M.p. 126–127°C. Anal. Found: C, 40.4; H, 6.0. C<sub>16</sub>H<sub>28</sub>O<sub>2</sub>PS<sub>2</sub>ClRu Calc.: C, 39.7; H, 5.8%. <sup>1</sup>H NMR  $\delta$ : 1.33 (d, 7 Hz, CHMe<sub>2</sub>); 2.25 (s,

Me), 2.95 (septet, 7 Hz, CH <); 5.24 (d), 5.48 (d) (each 6 Hz, C<sub>6</sub>H<sub>4</sub>) [arene protons]; 1.22 (d), 1.37 (d) (each 6.2 Hz, OCHMe<sub>2</sub>); 4.66 (m), 4.92 (m) (each 6.2 Hz OCH <) [dithiophosphate ligand]. <sup>31</sup>P NMR  $\delta$ : 100.6.

[RuCl{SSP(O<sup>*n*</sup>Bu)<sub>2</sub>}( $\eta^6$ -*p*-cymene)] (1f). Recrystallized from diethylether–hexane mixture in 54% yield. M.p. 70–72°C. Anal. Found: C, 42.7; H, 5.8. C<sub>18</sub>H<sub>32</sub>O<sub>2</sub>PS<sub>2</sub>ClRu Calc.: C, 42.2; H, 6.3%. <sup>1</sup>H NMR  $\delta$ : 1.33 (d, 7 Hz, CHMe<sub>2</sub>); 2.25 (s, Me), 2.95 (septet, 7 Hz, CH <); 5.24 (d), 5.49 (d) (each 6 Hz, C<sub>6</sub>H<sub>4</sub>) [arene protons]; 0.86 (t), 0.96 (t) (each 7 Hz, Me); 1.31 (m), 1.44 (m) ( $\gamma$ -CH<sub>2</sub>); 1.56 (quartet), 1.70 (quartet), ( $\beta$ -CH<sub>2</sub>); 4.03 (m, OCH<sub>2</sub>–) [dithiophosphate ligand]. <sup>31</sup>P NMR  $\delta$ : 103.3.

[RuCl{SSP(O<sup>*s*</sup>Bu)<sub>2</sub>}( $\eta^6$ -*p*-cymene)] (1g). Recrystallized from diethylether–hexane mixture in 23% yield. M.p. 71°C. Anal. Found: C, 42.0; H, 5.8. C<sub>18</sub>H<sub>32</sub>O<sub>2</sub>PS<sub>2</sub>ClRu Calc.: C, 42.2; H, 6.3%. <sup>1</sup>H NMR  $\delta$ : 1.32 (d, 7 Hz, CHMe<sub>2</sub>); 2.25 (s, Me), 2.94 (septet, 7 Hz, CH <); 5.23 (br, m), 5.48 (broad) (C<sub>6</sub>H<sub>4</sub>) (due to overlapping resonances attributable to *meso*, *RR* and *SS* forms, broad signals were observed) [arene protons]; 0.85 (t), 0.98 (t) (each 7.5 Hz, OCH–CH<sub>2</sub>Me); 1.21 (d), 1.37 (d) (each 6.2 Hz, OCH <<sub>Me</sub>); 1.42–1.78 (m, OCH–CH<sub>2</sub>–); 4.46 (m), 4.74 (m) OCH <. <sup>31</sup>P NMR  $\delta$ : 101.3.

### 3.2. Preparation of [Ru{SSP(OEt)<sub>2</sub>}(*p*-cymene)] (2)

To an ethanol (5 ml) solution of NH<sub>4</sub>SSP(OEt)<sub>2</sub> (204 mg, 1.00 mmol) diluted with CH<sub>2</sub>Cl<sub>2</sub>/diethylether (1 : 1 v/v, 20 ml) was added solid [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (134 mg, 0.22 mmol). The mixture was stirred at room temperature for 5 h. The solvents were evaporated in vacuo. The residue was treated with diethyl ether and water. The organic layer was separated, washed with water, dried over CaCl<sub>2</sub>, filtered, and evaporated in vacuo. The residue was recrystallized from ether/hexane mixture as brown crystals (139 mg, 52%). M.p. 78°C. Anal. Found: C, 35.3; H, 5.1. C<sub>18</sub>H<sub>34</sub>O<sub>4</sub>S<sub>4</sub>P<sub>2</sub>Ru Calc.: C, 35.7; H, 5.6%. <sup>1</sup>H NMR  $\delta$ : 1.29 (d, 7 Hz, CHMe<sub>2</sub>); 2.25 (s, Me), 2.92 (septet, 7 Hz, CH <); 5.44 (d), 5.72 (d) (each 6 Hz, C<sub>6</sub>H<sub>4</sub>) [arene protons]; 1.24 (t), 1.40 (t) (each corresponding to one Me, 7 Hz, OCCCH<sub>3</sub>); 1.34 (t, 7 Hz, 2Me, OCH<sub>2</sub>Me); 4.14 (m, OCH<sub>2</sub>– integrated for four CH<sub>2</sub> groups) [dithiophosphate protons]. <sup>31</sup>P NMR  $\delta$ : 113.6 (s), 98.1 (s).

### 3.3. Preparation of [Ru{SSP(OEt)<sub>2</sub>}(PPh<sub>3</sub>)( $\eta^6$ -*p*-cymene)] [BPh<sub>4</sub>] (3b)

To an acetone solution of [RuCl{SSP(OEt)<sub>2</sub>}(*p*-cymene)] (100.5 mg, 0.22 mmol) was added solid NaBPh<sub>4</sub> (76.7 mg, 0.22 mmol). The mixture was stirred at room temperature for 30 min. To this an acetone solution of PPh<sub>3</sub> (60.3 mg, 0.23 mmol) was added with stirring for

1 h, during which time the colour changed to orange–yellow. The solvent was evaporated in vacuo and the residue extracted with dichloromethane and filtered.

The filtrate was again concentrated in vacuo leaving a yellow–orange solid which was recrystallized from  $\text{CH}_2\text{Cl}_2$ /hexane mixture cooled in a freezer for three

Table 1

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Ru}\{\text{SSP}(\text{OEt})_2\}(\eta^6\text{-p-cymene})(\text{PPh}_3)][\text{BPh}_4]$

Atom	x	y	z	$U_{\text{eq}}$
Ru(1)	4974(1)	1937(1)	7576(1)	39(1)
P(1)	5043(1)	1385(1)	8727(1)	39(1)
S(1)	2857(1)	2324(1)	7671(1)	51(1)
S(2)	5619(1)	3613(1)	8539(1)	58(1)
P(2)	3815(2)	3708(1)	8116(1)	63(1)
O(1)	3237(5)	4450(3)	8687(4)	105(2)
O(2)	3857(6)	4217(4)	7419(3)	120(2)
C(1)	5900(6)	2345(4)	6650(3)	64(2)
C(2)	4668(7)	1872(5)	6244(3)	76(2)
C(3)	4213(5)	917(5)	6255(3)	68(2)
C(4)	5069(5)	496(3)	6705(3)	54(1)
C(5)	6328(5)	999(3)	7127(3)	49(1)
C(6)	6775(5)	1926(4)	7090(3)	53(1)
C(7)	8155(6)	2450(5)	7471(4)	87(2)
C(8)	2915(7)	315(10)	5737(4)	176(6)
C(9)	3051(8)	–74(10)	4826(4)	195(7)
C(10)	1980(10)	44(11)	5880(5)	224(8)
C(11)	4445(4)	63(3)	8334(3)	44(1)
C(12)	5242(5)	–621(4)	8367(3)	63(1)
C(13)	4752(7)	–1613(4)	7955(4)	85(2)
C(14)	3507(7)	–1935(4)	7521(4)	86(2)
C(15)	2705(6)	–1278(4)	7480(3)	64(1)
C(16)	3174(5)	–289(3)	7877(3)	48(1)
C(17)	6638(4)	1566(3)	9402(3)	45(1)
C(18)	6828(5)	1127(4)	10023(3)	59(1)
C(19)	8020(5)	1306(5)	10559(3)	66(2)
C(20)	9029(5)	1929(4)	10500(3)	65(1)
C(21)	8864(5)	2372(4)	9902(3)	63(1)
C(22)	7664(5)	2190(4)	9351(3)	54(1)
C(23)	4175(4)	1900(3)	9517(3)	42(1)
C(24)	4750(5)	2774(4)	10147(3)	58(1)
C(25)	4143(6)	3188(4)	10763(3)	68(2)
C(26)	2953(6)	2727(5)	10758(3)	69(2)
C(27)	2375(5)	1864(4)	10146(3)	68(2)
C(28)	2979(5)	1451(4)	9528(3)	57(1)
C(29)	2892(9)	4276(6)	9351(5)	115(3)
C(30)	1672(9)	4621(9)	9491(7)	166(5)
C(31)	2860(9)	4300(5)	6876(5)	110(3)
C(32)	2933(10)	5271(6)	6805(5)	129(3)
B(1)	1599(5)	2639(4)	3589(3)	44(1)
C(33)	728(4)	2855(3)	4281(3)	45(1)
C(34)	842(5)	2382(4)	4877(3)	62(1)
C(35)	172(6)	2554(5)	5494(4)	78(2)
C(36)	–618(6)	3236(6)	5559(4)	88(2)
C(37)	–745(6)	3722(5)	4996(5)	92(2)
C(38)	–80(5)	3534(4)	4375(4)	66(1)
C(39)	1135(4)	1511(3)	2919(3)	46(1)
C(40)	494(5)	722(4)	3080(4)	63(1)
C(41)	147(5)	–221(4)	2511(4)	78(2)
C(42)	410(5)	–415(4)	1752(4)	76(2)
C(43)	1047(6)	333(5)	1567(3)	76(2)
C(44)	1400(5)	1273(4)	2139(3)	63(1)
C(45)	1497(5)	3412(3)	3059(3)	49(1)
C(46)	2551(6)	4037(4)	3021(3)	62(1)
C(47)	2433(8)	4670(4)	2555(4)	83(2)
C(48)	1265(9)	4686(4)	2104(4)	91(2)
C(49)	196(7)	4076(5)	2111(4)	85(2)

Table 1 (continued)

Atom	x	y	z	$U_{eq}$
C(50)	323(6)	3449(4)	2573(3)	67(2)
C(51)	3100(4)	2796(3)	4101(3)	46(1)
C(52)	3949(5)	2176(4)	3897(4)	72(2)
C(53)	5239(6)	2400(6)	4323(4)	94(2)
C(54)	5712(6)	3233(6)	4978(4)	80(2)
C(55)	4909(6)	3857(5)	5210(4)	75(2)
C(56)	3631(5)	3633(4)	4781(3)	62(1)

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

days to give yellow crystals (102 mg, 46%). M.p. 185–188°C (decomp.). Anal. Found: C, 67.7; H, 6.1.  $C_{56}H_{59}O_2P_2S_2BRu$  Calc.: C, 67.1; H, 5.9%.  $^1H$  NMR

$\delta$ : 1.15 (d, 7 Hz,  $CHMe_2$ ); 1.80 (s, Me), 2.38 (septet, 7 Hz,  $CH <$ ); 4.90 (d), 5.06 (d) (each 6 Hz,  $C_6H_4$ ) [arene protons]; 0.92 (t), 1.37 (t) (each 7 Hz,  $OCCH_3$ ); 2.90,

Table 2

Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for  $[Ru(SSP(OEt)_2)(\eta^6\text{-p-cymene})(PPh_3)](BPh_4)$

Ru(1)–C(1)	2.234(5)	P(1)–C(11)	1.817(5)
Ru(1)–C(2)	2.247(5)	P(1)–C(17)	1.819(5)
Ru(1)–C(3)	2.257(5)	P(1)–C(23)	1.837(4)
Ru(1)–C(4)	2.211(4)		
Ru(1)–C(5)	2.204(4)	S(1)–P(2)	1.989(2)
Ru(1)–C(6)	2.261(5)	S(2)–P(2)	1.971(2)
		P(2)–O(1)	1.515(5)
Ru(1)–P(1)	2.3558(13)	P(2)–O(2)	1.599(5)
Ru(1)–S(1)	2.4312(14)	O(1)–C(29)	1.360(9)
Ru(1)–S(2)	2.431(2)	O(2)–C(31)	1.325(9)
C(1)–Ru(1)–C(2)	35.4(2)	C(1)–Ru(1)–S(2)	91.5(2)
C(1)–Ru(1)–C(3)	65.0(2)	C(2)–Ru(1)–S(2)	112.6(2)
C(1)–Ru(1)–C(6)	36.3(2)	C(3)–Ru(1)–S(2)	148.4(2)
C(2)–Ru(1)–C(3)	36.7(2)	C(4)–Ru(1)–S(2)	161.06(14)
C(2)–Ru(1)–C(6)	65.1(2)	C(5)–Ru(1)–S(2)	124.44(14)
C(3)–Ru(1)–C(6)	77.9(2)	C(6)–Ru(1)–S(2)	95.88(13)
C(4)–Ru(1)–C(1)	76.6(2)		
C(4)–Ru(1)–C(2)	65.4(2)	C(11)–P(1)–Ru(1)	107.71(14)
C(4)–Ru(1)–C(3)	36.5(2)	C(17)–P(1)–Ru(1)	115.6(2)
C(4)–Ru(1)–C(6)	65.8(2)	C(23)–P(1)–Ru(1)	120.83(14)
C(5)–Ru(1)–C(1)	65.2(2)		
C(5)–Ru(1)–C(2)	77.4(2)	P(1)–Ru(1)–S(1)	89.09(5)
C(5)–Ru(1)–C(3)	66.4(2)	P(1)–Ru(1)–S(2)	88.30(5)
C(5)–Ru(1)–C(4)	37.0(2)	S(2)–Ru(1)–S(1)	80.43(5)
C(5)–Ru(1)–C(6)	36.4(2)		
		P(2)–S(1)–Ru(1)	83.54(7)
C(1)–Ru(1)–P(1)	151.6(2)	P(2)–S(2)–Ru(1)	83.92(7)
C(2)–Ru(1)–P(1)	159.1(2)		
C(3)–Ru(1)–P(1)	122.5(2)	C(11)–P(1)–C(17)	105.9(2)
C(4)–Ru(1)–P(1)	95.20(14)	C(11)–P(1)–C(23)	106.3(2)
C(5)–Ru(1)–P(1)	91.79(12)	C(17)–P(1)–C(23)	99.1(2)
C(6)–Ru(1)–P(1)	115.49(13)		
		O(1)–P(2)–S(1)	116.7(2)
C(1)–Ru(1)–S(1)	118.8(2)	O(1)–P(2)–S(2)	117.1(2)
C(2)–Ru(1)–S(1)	93.4(2)	O(1)–P(2)–O(2)	99.0(3)
C(3)–Ru(1)–S(1)	92.38(14)	O(2)–P(2)–S(1)	113.6(2)
C(4)–Ru(1)–S(1)	118.16(14)	O(2)–P(2)–S(2)	105.2(2)
C(5)–Ru(1)–S(1)	155.13(13)	S(2)–P(2)–S(1)	104.88(8)
C(6)–Ru(1)–S(1)	155.14(13)	C(29)–O(1)–P(2)	120.8(5)
C(6)–Ru(1)–S(1)	155.14(13)	C(31)–O(2)–P(2)	127.2(6)

All the C–C bond distances are comparable with those reported for similar compounds, except C(8)–C(10) which is unusually short. Several attempts were made to relocate these atoms and also to constrain them, but the bond lengths after least-squares refinement return to the same value (1.14(1)  $\text{\AA}$ ).

4.04 (each doublet of quartets, 7 Hz (t), 10 Hz (d); OCH<sub>2</sub>); 6.81–6.99 (m), 7.31–7.55 (m) [PPh<sub>3</sub> + BPh<sub>4</sub>]. <sup>31</sup>P NMR δ: 35.7 (d, 23 Hz, PPh<sub>3</sub>); 80.2 (d, 23 Hz, SSP(OEt)<sub>2</sub>). Other complexes were prepared similarly and pertinent data are given below.

[Ru(SSP(OEt)<sub>2</sub>)(py)(η<sup>6</sup>-*p*-cymene)][BPh<sub>4</sub>] (**3a**). Recrystallized from acetone–dichloromethane–hexane mixture in 53% yield. M.p. 105–108°C (decomp.). Anal. Found: C, 62.5; H, 5.8; N, 2.0. C<sub>43</sub>H<sub>49</sub>NPO<sub>2</sub>S<sub>2</sub>BRu Calc.: C, 63.1; H, 6.0; N, 1.7%. <sup>1</sup>H NMR δ: 1.10 (d, 7 Hz, CHMe); 1.53 (s, Me), 2.40 (septet, 7 Hz, CH <); 4.69 (d), 5.00 (d) (each 6 Hz, C<sub>6</sub>H<sub>4</sub>) [arene protons]; 0.77 (t), 1.33 (t) (each 7 Hz, OC–CH<sub>3</sub>); 3.00, 4.02 (each doublet of quartets, 7 Hz (t), 9.5 Hz (d); OCH<sub>2</sub>); 6.86–7.04 (m), 7.43 (br, m), 8.33 (d,d, 5, 1.3 Hz) [Ph + py]. <sup>31</sup>P NMR δ: 102.7.

[Ru(SSP(OEt)<sub>2</sub>)(4-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P}(η<sup>6</sup>-*p*-cymene)][BPh<sub>4</sub>] (**3c**). Recrystallized from dichloromethane–hexane mixture in 44% yield. M.p. 155–157°C. Anal. Found: C, 64.1; H, 5.8. C<sub>56</sub>H<sub>56</sub>F<sub>3</sub>O<sub>2</sub>P<sub>2</sub>S<sub>2</sub>BRu Calc.: C, 63.7; H, 5.3%. <sup>1</sup>H NMR δ: 1.14 (d, 7 Hz, CHMe<sub>2</sub>); 1.69 (s, Me), 2.38 (septet, 7 Hz, CH <); 4.82 (d), 5.01 (d) (each 6 Hz, C<sub>6</sub>H<sub>4</sub>) [arene protons]; 0.99 (t), 1.37 (t) (each 7 Hz, OCCH<sub>3</sub>); 3.11, 4.03 (each doublet of quartets, 7 Hz (t), 10 Hz (d); OCH<sub>2</sub>); 6.80–7.37 (m) [Ph + C<sub>6</sub>H<sub>4</sub>F]. <sup>31</sup>P NMR δ: 35.1 [d, 22, P(C<sub>6</sub>H<sub>4</sub>F-4)<sub>3</sub>]; 82.3 [d, 22 Hz, SSP(OEt)<sub>2</sub>].

[Ru(SSP(OEt)<sub>2</sub>)(AsPh<sub>3</sub>)(η<sup>6</sup>-*p*-cymene)][BPh<sub>4</sub>] (**3d**). Recrystallized from dichloromethane–hexane mixture in 51% yield. M.p. 176–178°C. Anal. Found: C, 64.0; H, 6.0. C<sub>56</sub>H<sub>59</sub>AsPO<sub>2</sub>S<sub>2</sub>BRu Calc.: C, 64.3; H, 5.7%. <sup>1</sup>H NMR δ: 1.07 (d, 7 Hz, CHMe<sub>2</sub>); 1.83 (s, Me), 2.23 (septet, 7 Hz, CH <); 5.01 (d), 5.10 (d) (each 6 Hz, C<sub>6</sub>H<sub>4</sub>) [arene protons]; 0.86 (t), 1.36 (t) (each 7 Hz, OCCH<sub>3</sub>); 2.78, 4.04 (doublet of quartets, 7 Hz (t), 10 Hz (d); OCH<sub>2</sub>); 6.81–6.99 (m), 7.31–7.51 (m) [Ph]. <sup>31</sup>P NMR δ: 79.3 (s).

#### 4. Crystallography

Yellow needle-shaped single crystals of [Ru(*p*-cymene){SSP(OEt)<sub>2</sub>}(PPh<sub>3</sub>)] [BPh<sub>4</sub>] were selected for X-ray single crystal diffraction data collection. All the measurements were performed at room temperature (295 K) on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo K α radiation (λ = 0.7107 Å) employing the ω–2θ scan technique. The unit cell parameters were determined from 25 randomly selected reflections using automatic searching procedure, indexing and least-squares refinement routines. The data were corrected for Lorentz and polarization effects. The data were monitored by measuring two standard reflections, (1 5 – 8) and (–4 – 1 – 5), every 60 min of X-ray exposure time. The structure was solved by the heavy

Table 3

Crystal data and structure refinement for [Ru(SSP(OEt)<sub>2</sub>)(η<sup>6</sup>-*p*-cymene)(PPh<sub>3</sub>)] [BPh<sub>4</sub>]

Empirical formula	C <sub>56</sub> H <sub>59</sub> P <sub>2</sub> S <sub>2</sub> O <sub>2</sub> BRu
Formula weight	1002.05
Temperature	293 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
Unit cell dimensions	$a = 10.756(3)$ Å $\alpha = 107.23(3)^\circ$ $b = 14.468(5)$ Å $\beta = 101.31(3)^\circ$ $c = 17.387(5)$ Å $\gamma = 96.73(3)^\circ$
Volume	2489.3(13) Å <sup>3</sup>
Z	2
Absorption coefficient	0.504 mm <sup>-1</sup>
<i>F</i> (000)	1044
Crystal size	0.38 × 0.35 × 0.22 mm <sup>3</sup>
θ range for data collection	2.06 to 24.93
Reflections collected	6952
Independent reflections	6543 [ <i>R</i> <sub>int</sub> = 0.0098]
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	6543/0/582
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.997
Final <i>R</i> indices	<i>R</i> <sub>1</sub> = 0.0430, <i>wR</i> <sub>2</sub> = 0.1116
[ <i>I</i> > 2σ( <i>I</i> )]	
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0490, <i>wR</i> <sub>2</sub> = 0.1185
Largest difference peak and hole	1.323 and –0.661 e Å <sup>-3</sup>

atom method of the SHELXS-86 program [25], and structure refinement was carried using the SHELXL-93 program [26]. PLUTO [27] was used for the molecular plotting.

The positions of hydrogen atoms were located partly from the difference electron density maps and also using the geometrical method of AFIX instruction in the SHELXL-93 program. The weighting scheme employed was of the form  $w = 1.0 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ , where  $P = (F_o^2 + 2F_c^2) / 3$  and *a* and *b* were refined to values of 0.0596 and 5.790 respectively. All the calculations were carried out on a NORISK-DATA (ND-500) computer and an IBM compatible PC-AT 486 system.

The crystallographic data together with data collection details are given in Table 3.

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