

# $(\mu$ -Diphenylphosphido- $\kappa P:P$ )- $\mu$ -hydrido-( $\mu$ -4-hydroxybenzenethiolato- $\kappa^2 S:S$ )bis[( $\eta^6$ -hexamethylbenzene)ruthenium(II)] tetrafluoroborate

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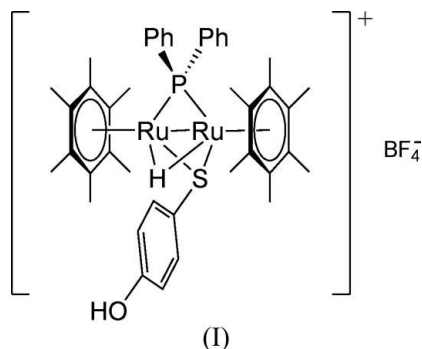
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The new triple-bridged dinuclear cation  $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-}p\text{-S-C}_6\text{H}_4\text{-OH})(\mu_2\text{-PPh}_2)(\mu_2\text{-H})]^+$ , isolated and characterized as the tetrafluoroborate salt, was prepared by reacting the precursor  $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_2(\mu_2\text{-PPh}_2)](\text{BF}_4)$  and *p*-hydroxythiophenol in refluxing ethanol. The single-crystal X-ray structure analysis of  $[(\eta^6\text{-C}_{12}\text{H}_{18})_2\text{Ru}_2(\mu_2\text{-S-C}_6\text{H}_4\text{-OH})(\mu_2\text{-H})(\mu_2\text{-P}(\text{C}_6\text{H}_5)_2)](\text{BF}_4)$  shows the formation of the *meso* form; despite the two stereogenic centres the complex is not chiral.

## Comment

The synthesis of  $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-}p\text{-S-C}_6\text{H}_4\text{-OH})(\mu_2\text{-PPh}_2)(\mu_2\text{-H})]^+\text{BF}_4^-$  (I), was carried out by reacting  $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_2(\mu_2\text{-PPh}_2)](\text{BF}_4)$  (Tschan *et al.*, 2005) and *p*-hydroxythiophenol in refluxing ethanol. The best yield (30%) was obtained by using two equivalents of *p*-hydroxythiophenol.



In the cation of (I), each Ru atom is coordinated by an  $\eta^6\text{-C}_6\text{Me}_6$  ligand, a bridging P atom, a bridging S atom and a bridging H atom. The molecular structure of (I) is depicted in Fig. 1, and significant bond lengths and bond angles are listed in Table 1. Despite the presence of two stereogenic ruthenium centres, the complex is not chiral. The Ru–Ru distance [2.8522 (4) Å] is in accordance with a metal–metal single bond. The presence of two phenyl groups on the phosphorus bridging ligand forces the arene–Ru–Ru–arene system to adopt a distorted geometry. The angle between the two  $\text{C}_6\text{Me}_6$  arene ligands is 37.38 (14)°. The C1–P1–Ru1–Ru2 torsion angle is 118.15 (13)° and the C7–P1–Ru1–Ru2 torsion angle is –116.95 (13)°. The distances between the metal and the associated ring centroid are similar for both Ru atoms

(1.75 Å for Ru1 and 1.76 Å for Ru2). The Ru–C distances fall in the range 2.185 (3)–2.337 (3) Å for the  $\text{C}_6\text{Me}_6$  arene ligands, with an average Ru–C distance of 2.26 (5) Å. The structure presents intermolecular hydrogen bonds between the

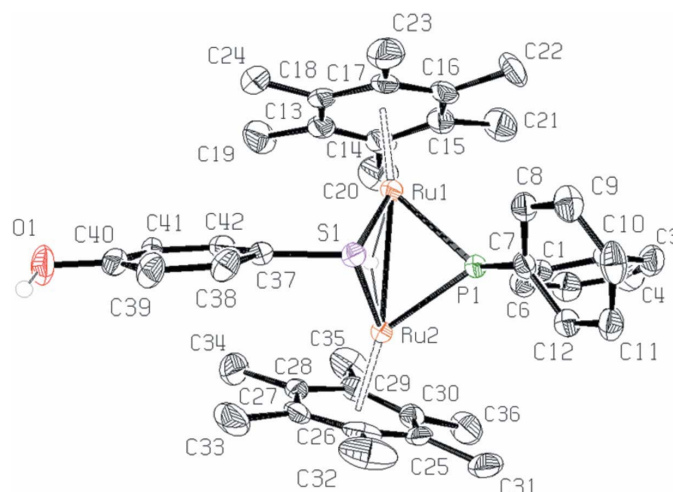


Figure 1

The molecular structure of (I). The tetrafluoroborate anion and the CH H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

hydroxyl H atom and two F atoms of the counter anion  $\text{BF}_4^-$  (Table 2).

## Experimental

The reaction was carried out under a nitrogen atmosphere, using standard Schlenk techniques, and solvents were nitrogen-saturated prior to use. *p*-Hydroxythiophenol was purchased from Aldrich and used as received. A brown solution of  $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_2(\mu_2\text{-PPh}_2)](\text{BF}_4)$  (200 mg, 0.25 mmol) and *p*-hydroxythiophenol (63 mg, 0.5 mmol) in ethanol (60 ml, puriss.) was refluxed for 18 h. After cooling to room temperature, the solvent was evaporated to dryness. The brown–red solid was dissolved in dichloromethane and filtered through celite in order to eliminate an insoluble brown residue. After evaporation of the dichloromethane, the red solid was washed with diethyl ether (3 × 40 ml) and purified by preparative thin-layer chromatography on silica (eluent acetone/dichloromethane 3:10). The product was extracted with acetone from the red band, and evaporation of the solvent gave the pure product (I) (yield 30%, 0.076 mmol, 70 mg). Red crystals suitable for single-crystal X-ray analysis were obtained by slow diffusion of hexane into a concentrated acetone solution of (I).

The two phenyl substituents at the P atom in (I) are not equivalent, owing to the tetrahedral geometry of the S atom, which gives rise to eight signals in the  $^{13}\text{C}$  NMR spectrum. In the  $^1\text{H}$  NMR spectrum, the signal of the hydrido ligand at  $\delta = -14.08$  p.p.m. (doublet) is deshielded with respect to that found for the precursor  $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{-Ru}_2(\mu_2\text{-H})_2(\mu_2\text{-PPh}_2)]^+$  (Tschan *et al.*, 2005) and shielded with respect to that found for the related complex  $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-P-S-C}_6\text{H}_4\text{-Br})_2(\mu_2\text{-H})]^+$  (Tschan *et al.*, 2004).

#### Crystal data

$[\text{Ru}_2(\text{C}_6\text{H}_5\text{OS})(\text{C}_{12}\text{H}_{10}\text{P})\text{H}(\text{C}_{12}\text{H}_{18})_2]\text{BF}_4$	$V = 3991.0$ (5) $\text{\AA}^3$
$M_r = 924.82$	$Z = 4$
Monoclinic, $P2_1/n$	$D_x = 1.539$ $\text{Mg m}^{-3}$
$a = 11.2081$ (7) $\text{\AA}$	Mo $K\alpha$ radiation
$b = 15.0744$ (11) $\text{\AA}$	$\mu = 0.90$ $\text{mm}^{-1}$
$c = 23.6220$ (16) $\text{\AA}$	$T = 173$ (2) K
$\beta = 90.315$ (8) $^\circ$	Block, red
	$0.50 \times 0.15 \times 0.10$ mm

#### Data collection

Stoe IPDS diffractometer	7664 independent reflections
$\varphi$ scans	4812 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{\text{int}} = 0.077$
30321 measured reflections	$\theta_{\text{max}} = 25.9^\circ$

#### Refinement

Refinement on $F^2$	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.032$	$w = 1/[\sigma^2(F_o^2) + (0.0231P)^2]$
$wR(F^2) = 0.062$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.81$	$(\Delta\rho)_{\text{max}} = 0.001$
7664 reflections	$\Delta\rho_{\text{max}} = 0.55$ $\text{e \AA}^{-3}$
486 parameters	$\Delta\rho_{\text{min}} = -0.77$ $\text{e \AA}^{-3}$

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

C1—P1	1.827 (4)	P1—Ru2	2.3092 (9)
C7—P1	1.827 (3)	Ru1—S1	2.3685 (9)
C37—S1	1.787 (3)	Ru1—Ru2	2.8522 (4)
C40—O1	1.370 (4)	Ru2—S1	2.3740 (8)
P1—Ru1	2.2957 (9)		
C7—P1—C1	102.02 (16)	Ru1—P1—Ru2	76.54 (3)
C7—P1—Ru1	119.04 (11)	C37—S1—Ru1	110.87 (11)
C1—P1—Ru1	118.47 (10)	C37—S1—Ru2	106.45 (10)
C7—P1—Ru2	119.89 (11)	Ru1—S1—Ru2	73.94 (3)
C1—P1—Ru2	120.95 (11)		

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
O1—H1O $\cdots$ F2 <sup>i</sup>	0.84	2.12	2.841 (4)	144
O1—H1O $\cdots$ F3 <sup>i</sup>	0.84	2.40	3.190 (4)	157

Symmetry code: (i)  $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ .

All CH and OH H atoms were included in calculated positions (C—H = 0.95  $\text{\AA}$  for  $\text{CH}_{\text{arom}}$  and 0.98  $\text{\AA}$  for  $\text{CH}_3$ ; O—H = 0.84  $\text{\AA}$ ) and treated as riding atoms with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ . The methyl and hydroxyl groups were allowed to rotate but not to tip. The hydride atom was located in a difference map and refined isotropically; Ru1—H1H = 1.72 (3) and Ru2—H1H = 1.83 (3)  $\text{\AA}$ .

Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 2000); cell refinement: *CELL* in *IPDS Software*; data reduction: *INTEGRATE* in *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-32* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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