

# Synthesis and characterization of pentamethylcyclopentadienyl–rhodium(III) dialkyldithiophosphate complexes: single-crystal structure of $[\text{Cp}^*\text{RhCl}\{\text{S}_2\text{P}(\text{OEt})_2\}]$

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## Abstract

Reactions of  $[\text{Cp}^*\text{Rh}(\mu\text{-Cl})\text{Cl}]_2$  with  $\text{NH}_4\text{S}_2\text{P}(\text{OR})_2$  in 1:1 and 1:2 stoichiometry gave complexes of the type  $[\text{Cp}^*\text{RhCl}\{\text{S}_2\text{P}(\text{OR})_2\}]$  (**1**) ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ;  $\text{R} = \text{Et}, \text{Pr}^i, \text{Pr}^t$ ) and  $[\text{Cp}^*\text{Rh}\{\text{S}_2\text{P}(\text{OR})_2\}_2]$  (**2**) ( $\text{R} = \text{Et}$ ). Complex **1** on treatment with  $\text{AgSO}_3\text{CF}_3$  in acetone followed by addition of a neutral donor ligand (L) gave cationic complexes,  $[\text{Cp}^*\text{Rh}\{\text{S}_2\text{P}(\text{OR})_2\}\text{L}][\text{SO}_3\text{CF}_3]$  (**3**) [ $\text{R} = \text{Et}$ ;  $\text{L} = \text{PPh}_3$ ;  $\text{P}(\text{C}_6\text{H}_4\text{Me-4})_3 = (\text{Ptol}_3)$ ,  $\text{AsPh}_3$ ]. All the complexes **1–3** have been characterized by elemental analysis, electronic spectra, IR and NMR ( $^1\text{H}$ ,  $^{31}\text{P}$ ) data. The structure of one of the complexes,  $[\text{Cp}^*\text{RhCl}\{\text{S}_2\text{P}(\text{OEt})_2\}]$  (**1a**) has been established unambiguously by single-crystal X-ray analysis. The structure consists of a central rhodium atom coordinated to a  $\eta^5$ -pentamethylcyclopentadienyl ligand, a chelated dithiophosphate and a chloride ligand. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Dialkyldithiophosphate; Crystal structure; NMR; Pentamethylcyclopentadienyl–rhodium; Rhodium

## 1. Introduction

During the last three decades or so, considerable work has been done on classical coordination complexes of platinum group metals with dithioacid ligands ( $\text{R}_2\text{NCS}_2$ ,  $\text{ROCS}_2$ ,  $\text{RCS}_2$ ,  $\text{R}_2\text{PS}_2$  and  $(\text{RO})_2\text{PS}_2$ ) [1,2]. However, in recent years a number of organometallic derivatives of these ligands have been isolated and characterized by us [3–10] and others [11,12]. Some of these organometallic derivatives show unusual properties when compared to their classical coordination complexes.

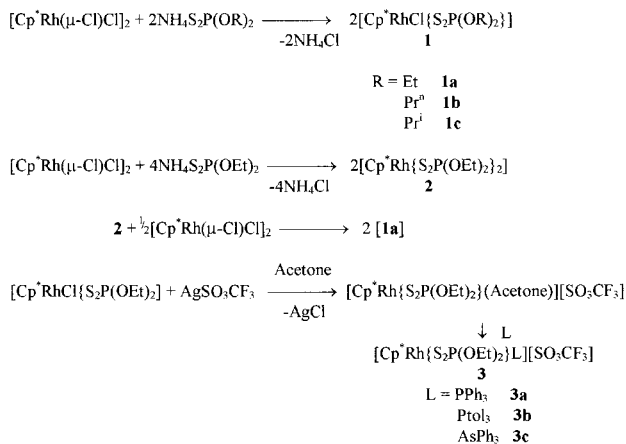
Pentamethylcyclopentadienyl–rhodium complexes with sulfur ligands are of much current interest [13–16]. However, complexes with dithio ligands are rare [17,18]. A few  $\text{Cp}^*\text{Rh}(\text{III})$  complexes with dithiophosphinic acids and dithiocarbamates have been reported by Robertson and Stephenson [18]. This study deals with the synthesis and characterization of  $\text{Cp}^*\text{Rh}(\text{III})$  complexes with dithiophosphoric acids.

## 2. Results and discussion

Treatment of  $[\text{Cp}^*\text{Rh}(\mu\text{-Cl})\text{Cl}]_2$  with ammonium salts of dialkyldithiophosphoric acid in 1:1 and 1:2 stoichiometry resulted in almost quantitative formation of  $[\text{Cp}^*\text{RhCl}\{\text{S}_2\text{P}(\text{OR})_2\}]$  (**1**) and  $[\text{Cp}^*\text{Rh}\{\text{S}_2\text{P}(\text{OR})_2\}_2]$  (**2**), respectively (Scheme 1) as brown-coloured crystalline solids. The complex **1a** can readily be obtained in quantitative yield by the reaction of **2** with  $[\text{Cp}^*\text{Rh}(\mu\text{-Cl})\text{Cl}]_2$ . The complex **1a** on treatment with  $\text{AgSO}_3\text{CF}_3$  followed by addition of a neutral donor ligand in acetone afforded  $[\text{Cp}^*\text{Rh}\{\text{S}_2\text{P}(\text{OR})_2\}\text{L}][\text{SO}_3\text{CF}_3]$  (**3**) as yellow solids.

The electronic spectra of these complexes, except **2**, in benzene displayed three absorptions in the region 282–445 nm. The absorption at ca. 325 nm may be assigned to the  $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$  transition. This band in **1–3** was not much affected by changes in the ligands around the ‘ $\text{Cp}^*\text{Rh}$ ’ fragment. However, substituent effects were reflected in the absorption appearing at longer wavelength (368–445 nm). This absorption may be attributed to the first spin-allowed ligand-field band

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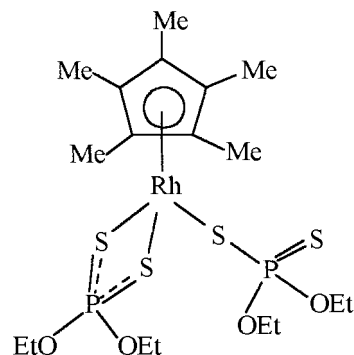


Scheme 1.

( $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ ). When chloride in **1** is substituted by a dithio ligand (e.g. as in **2**) or a neutral ligand (e.g. as in cationic complexes, **3**), the absorption maximum was blue shifted. The electronic spectra of tris–dithio complexes of Rh(III) have been reported earlier [1,19].

The IR spectra were interpreted by comparing the spectra of these complexes with those of  $[\text{Cp}^*\text{RhCl}]_2$ , free acids and their metal complexes reported from our laboratory. The bands in the regions 950–1105 and 750–790  $\text{cm}^{-1}$  may be assigned to  $\nu(\text{P})\text{-O-C}$  and  $\nu\text{P-O-(C)}$ , respectively [20]. The  $\nu\text{P-S}$  stretchings have been assigned in the region 635–660  $\text{cm}^{-1}$ . The P–S and P=S stretching frequencies which can give some information regarding various structural possibilities generally appear in the same region for free acids, their esters and metal complexes and thus have limited diagnostic utility [21]. A weak absorption in **1** at 279–290  $\text{cm}^{-1}$  may be assigned to  $\nu\text{Rh-Cl}$  [1,18].

The  $^1\text{H-NMR}$  spectra of **1–3** showed the characteristic resonances and peak multiplicities for the groups attached to rhodium. The spectra exhibited a sharp singlet for the Cp\* protons. The alkoxy groups of the dithio ligand in **1** and **3** displayed two separate sets of resonances indicating non-equivalence of the OR groups. In **1**, the  $\alpha$ -protons are not well resolved in  $\text{CDCl}_3$  solution, however, in benzene-*d*<sub>6</sub> solution these signals could be resolved. One set of resonances (the down field signals) are not much affected on changing chloride in **1** with a neutral donor ligand in **3**. The ligand dependence of the high-field resonances may be attributed to the chemical shift anisotropy due to the aromatic rings of the neutral donor ligands in **3**. This has been demonstrated by the structure of  $[\text{Ru}\{\text{S}_2\text{P}(\text{OEt})_2\}(\eta^6\text{-}p\text{-cymene})(\text{PPh}_3)][\text{BPh}_4]$  in which one of the OEt group lies down the arene ring and is parallel to one of the phenyl rings of  $\text{PPh}_3$ , while the second OEt group remains outside the ring currents and hence is slightly affected [8]. The  $^1\text{H-NMR}$  spectrum of **2** showed three sets of dithio ligand proton

Fig. 1. Structure of **2**.

signals assignable to bidentate and monodentate ligand moieties. For the monodentate dithio ligand, only one set of resonances have been observed. The Cp\* methyl protons in **3a** and **3b** appeared as doublets ( $^4J(\text{P-H})$  ca. 3.5 Hz) owing to the coupling with the phosphorus of the  $\text{PR}_3$  ligand [14,22].

The  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of **1** exhibited a doublet with  $^2J(^{103}\text{Rh}\text{-}^{31}\text{P})$  of ca. 13 Hz due to the dithiophosphate ligand. Similarly, the spectra of **3** containing phosphine ligands displayed two doublets of doublets due to the coupling with  $^{103}\text{Rh}$  and  $^{31}\text{P}$  nuclei. They were attributed to the dithiophosphate and phosphine ligands. The magnitude of  $^1J(^{103}\text{Rh}\text{-}^{31}\text{P})$  (145 Hz),  $^2J(^{103}\text{Rh}\text{-}^{31}\text{P})$  (ca. 11 Hz) and  $^3J(^{31}\text{P}\text{-}^{31}\text{P})$  (ca. 18 Hz) couplings are in agreement with the values reported earlier [14,22]. Substitution of chloride in **1** with neutral donor ligands resulted in a considerable shielding of the  $^{31}\text{P}$  resonance indicating reduced electron density at rhodium. The  $^{31}\text{P-NMR}$  spectrum of **2** displayed a doublet with  $^2J(^{103}\text{Rh}\text{-}^{31}\text{P})$  13 Hz at  $\delta$  93.8 for the chelating dithio ligand and a singlet at  $\delta$  112.8 for the monodentate dithio group (Fig. 1).

The molecular structure of **1a** was unambiguously determined by X-ray crystallography. An ORTEP drawing of **1a** is shown in Fig. 2 with selected bond lengths and angles in Table 1. The molecular structure consists

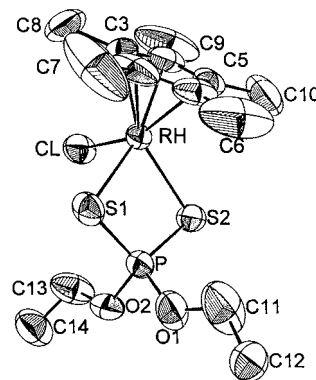
Fig. 2. Molecular structure of  $[\text{Cp}^*\text{RhCl}\{\text{S}_2\text{P}(\text{OEt})_2\}]$  (**1a**) with crystallographic numbering scheme.

Table 1  
Selected bond lengths (Å) and angles (°) for [Cp\*RhCl{S<sub>2</sub>P(OEt)<sub>2</sub>}] (1a)

Bond length (Å)			
Rh–C(1)	2.125(5)	Rh–S(1)	2.440(2)
Rh–C(2)	2.129(5)	Rh–S(2)	2.4270(13)
Rh–C(3)	2.125 (6)	P–S(1)	1.985(2)
Rh–C(4)	2.151 (5)	P–S(2)	1.985(2)
Rh–C(5)	2.153(5)	P–O(1)	1.563(4)
Rh–Cl	2.409(2)	P–O(2)	1.579(4)
Bond angles (°)			
C(1)–Rh–C(2)	40.1(3)	C(4)–Rh–S(1)	158.2(2)
C(1)–Rh–C(3)	65.3(3)	C(5)–Rh–S(1)	142.2(2)
C(1)–Rh–C(4)	63.9(2)	C(1)–Rh–S(2)	104.4(2)
C(1)–Rh–C(5)	38.3(2)	C(2)–Rh–S(2)	142.3(3)
C(2)–Rh–C(3)	38.9(3)	C(3)–Rh–S(2)	156.1(2)
C(2)–Rh–C(4)	63.7(3)	C(4)–Rh–S(2)	119.4(2)
C(2)–Rh–C(5)	64.0(2)	C(5)–Rh–S(2)	96.1(2)
C(3)–Rh–C(4)	37.0(3)	Cl–Rh–S(1)	92.68(5)
C(3)–Rh–C(5)	62.1(2)	Cl–Rh–S(2)	90.96(5)
C(4)–Rh–C(5)	36.4(2)	S(1)–Rh–S(2)	80.99(5)
C(1)–Rh–Cl	157.7(2)	P–S(1)–Rh	86.46(6)
C(2)–Rh–Cl	126.7(3)	P–S(2)–Rh	86.82(6)
C(3)–Rh–Cl	94.2(2)	O(1)–P–O(2)	94.8(3)
C(4)–Rh–Cl	94.6(2)	O(1)–P–S(1)	115.4(3)
C(5)–Rh–Cl	125.2(2)	O(2)–P–S(1)	113.3(2)
C(1)–Rh–S(1)	105.5(2)	O(1)–P–S(2)	114.0(2)
C(2)–Rh–S(1)	95.6(2)	O(2)–P–S(2)	114.1(2)
C(3)–Rh–S(1)	122.0(2)	S(1)–P–S(2)	105.51(8)

of discrete monomeric molecules with distorted octahedral configuration around the rhodium atom having a pentamethylcyclopentadienyl ring at one face. The thermal ellipsoids of the methyl groups attached to the cyclopentadienyl ring indicate nearly free liberation of the cyclopentadienyl ring about the axis normal to its plane. The Cp\*Rh fragment is coordinated with sulfur atoms of a symmetrically chelated dithiophosphate group and a chloride ligand. The rhodium atom is situated 1.775 Å above the center of the planar Cp\* ring. All η<sup>5</sup>-Cp\*Rh bond distances are ordinary and are approximately equal with an average value of 2.137 Å and a range of 2.125(6)–2.153(5) Å [23]. One of the right angles around rhodium, S(1)–Rh–S(2), is considerably reduced (80.99(5)°) owing to the small bite of the dithio ligand. The two Rh–S bond distances (2.427(1) and 2.440(2) Å) [14–16,24] and Rh–Cl (2.409 Å) [15,16] are in good agreement with the values reported for [Cp\*Rh(μ-SH)Cl]<sub>2</sub> and other related complexes.

The P–S bond lengths of 1.985 Å are intermediate between the double (1.94 Å) and the single bond values (2.09 Å) indicating partial double bond character as expected. The four-membered chelate ring RhS<sub>2</sub>P is planar (the phosphorus atom shows maximum deviation 0.04 Å from the plane formed by the Rh, S(1), S(2), P atoms). In metal complexes, the four-membered ring has been shown to adopt either a planar [6,8] or a

non-planar [3] conformation. The four-membered chelate ring and the Cp\* ring are inclined at the angle of 124.3°.

### 3. Experimental

The ammonium salt of dithiophosphoric acids [25] and [Cp\*Rh(μ-Cl)Cl]<sub>2</sub> [26] were prepared according to reported procedures. All the preparations were carried out under nitrogen atmosphere. The elemental analysis for C and H were carried out in the Analytical Chemistry Division of this research centre. The electronic spectra of these complexes were recorded in anhydrous benzene in the region 250–800 nm on a Shimadzu UV-160 A. The infrared spectra were recorded as Nujol mulls between CsI plates on a Bomem MB-102 FT-IR spectrometer. The <sup>1</sup>H- and <sup>31</sup>P{<sup>1</sup>H}-NMR spectra were recorded in CDCl<sub>3</sub> in 5 mm tubes on a Bruker DPX-300 NMR spectrometer operating at 300 and 121.42 MHz, respectively. The chemical shifts are relative to internal solvent peak (CHCl<sub>3</sub>, δ 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 [Cp\*RhCl{S<sub>2</sub>P(OEt)<sub>2</sub>}] (1a)

To a dichloromethane solution (10 ml) of [Cp\*Rh(μ-Cl)Cl]<sub>2</sub> (135 mg, 0.22 mmol), solid NH<sub>4</sub>S<sub>2</sub>P(OEt)<sub>2</sub> (90 mg, 0.44 mmol) was added and the mixture stirred at room temperature for 3 h. The precipitated ammonium chloride was filtered off and the filtrate was concentrated in vacuo to give a brown solid which was recrystallized from dichloromethane–hexane mixture in 81% (162 mg) yield. M.p. 169–170°C. Found: C, 36.6; H, 5.5. Anal. Calc. C<sub>14</sub>H<sub>25</sub>ClO<sub>2</sub>PS<sub>2</sub>Rh: C, 36.7; H, 5.5%. Electronic spectrum: λ<sub>max</sub> 285 (ε 4172 M<sup>-1</sup> cm<sup>-1</sup>), 330 (ε 2557 M<sup>-1</sup> cm<sup>-1</sup>), 445 nm (ε 2682 M<sup>-1</sup> cm<sup>-1</sup>). <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub> δ): 1.14, 1.19 (each t, 7 Hz, OCH<sub>2</sub>Me); 1.44 (s, C<sub>5</sub>Me<sub>5</sub>); 4.06, 4.51 (each dq; 10 Hz (d), 7 Hz (q)). <sup>1</sup>H-NMR (CDCl<sub>3</sub> δ): 1.25, 1.38 (each t, 7 Hz, OCH<sub>2</sub>Me); 1.73 (s, C<sub>5</sub>Me<sub>5</sub>); 4.13 (m, OCH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H}-NMR (C<sub>6</sub>D<sub>6</sub> δ): 99.4 (d, <sup>2</sup>J(<sup>103</sup>Rh–<sup>31</sup>P) 12.7 Hz); <sup>31</sup>P{<sup>1</sup>H}-NMR (CDCl<sub>3</sub> δ): δ: 98.2 (d, <sup>2</sup>J(<sup>103</sup>Rh–<sup>31</sup>P) 12.9 Hz).

Complexes **1b** and **1c** were prepared similarly and their pertinent data are given below.

##### 3.1.1. [Cp\*RhCl{S<sub>2</sub>P(OPr<sup>n</sup>)<sub>2</sub>}] (1b)

Recrystallized from benzene–hexane. M.p. 114°C. Found: C, 38.5; H, 5.8. Anal. Calc. C<sub>16</sub>H<sub>29</sub>ClO<sub>2</sub>PS<sub>2</sub>Rh: C, 39.5; H, 6.0%. Electronic spectrum λ<sub>max</sub>: 285 (ε 4320 M<sup>-1</sup> cm<sup>-1</sup>), 330 (ε 2668 M<sup>-1</sup> cm<sup>-1</sup>), 444 nm (ε 2630 M<sup>-1</sup> cm<sup>-1</sup>). <sup>1</sup>H-NMR (CDCl<sub>3</sub> δ): 0.88, 0.98 (each t, 7.4 Hz; OCH<sub>2</sub>CH<sub>2</sub>Me); 1.65–1.75 (m, OCH<sub>2</sub>CH<sub>2</sub>); 1.73 (s, C<sub>5</sub>Me<sub>5</sub>); 3.95–4.08 (m, OCH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H}-NMR (CDCl<sub>3</sub> δ): 98.7 (d, <sup>2</sup>J(<sup>103</sup>Rh–<sup>31</sup>P) 13.5 Hz).

### 3.1.2. $[Cp^*RhCl\{S_2P(OPr^i)_2\}]$ (**1c**)

Recrystallized from benzene–hexane. M.p. 161–162°C. Found: C, 39.3; H, 6.1. Anal. Calc.  $C_{16}H_{29}ClO_2PS_2Rh$ : C, 39.5; H, 6.0%. Electronic spectrum  $\lambda_{max}$ : 285 ( $\epsilon$  4549  $M^{-1} cm^{-1}$ ), 332 ( $\epsilon$  2873  $M^{-1} cm^{-1}$ ), 445 nm ( $\epsilon$  2965  $M^{-1} cm^{-1}$ ).  $^1H$ -NMR ( $CDCl_3$   $\delta$ ): 1.24, 1.35 (each d, 6.0 Hz,  $OCHMe_2$ ); 1.72 (s,  $C_5Me_5$ ); 4.70, 4.94 (each sextet, 6.0 Hz,  $OCH$ ).  $^{31}P\{^1H\}$ -NMR ( $CDCl_3$   $\delta$ ): 95.8 (d,  $^2J(^{103}Rh-^{31}P)$  13.0 Hz).

### 3.2. Preparation of $[Cp^*Rh\{S_2P(OEt)_2\}]$ (**2**)

This complex was prepared similarly to **1a** except that  $NH_4S_2P(OEt)_2$  was used in four equivalents. The product was recrystallized from hexane in 86% yield. M.p. 94°C. Found: C, 35.1; H, 5.8. Anal. Calc.  $C_{18}H_{35}O_4P_2S_4Rh$ : C, 35.5; H, 5.8%. Electronic spectrum  $\lambda_{max}$ : 329 ( $\epsilon$  5488  $M^{-1} cm^{-1}$ ) 428 (sh) nm.  $^1H$ -NMR ( $CDCl_3$   $\delta$ ): 1.25, 1.27, 1.36 (each t, 7 Hz, in 1:2:1 ratio,  $OCH_2Me$ ); 1.75 (s,  $C_5Me_5$ ); 4.03–4.14 (m,  $OCH_2$ ).  $^{31}P\{^1H\}$ -NMR ( $CDCl_3$   $\delta$ ): 93.8 (d,  $^2J(^{103}Rh-^{31}P)$  13 Hz); 112.8 (s).

### 3.3. Preparation of $[Cp^*Rh\{S_2P(OEt)_2\}(PPh_3)][SO_3CF_3]$ (**3a**)

To an acetone solution (5 ml) of  $AgSO_3CF_3$  (40 mg, 0.15 mmol), a solution of  $[Cp^*RhCl\{S_2P(OEt)_2\}]$  (70 mg, 0.15 mmol) in acetone was added with stirring for 15 min, during which time  $AgCl$  precipitated out. To this, solid triphenylphosphine (42 mg, 0.16 mmol) was added. The colour of the solution changed immediately to golden-yellow. The stirring continued further at room temperature for 4 h. The solution was centrifuged and filtered to remove  $AgCl$ . The filtrate was concentrated in vacuum to give an orange paste which on scratching in hexane (2–3 times) gave orange powder (90 mg, 71%). M.p. 180°C. Found: C, 47.4; H, 4.9. Anal. Calc.  $C_{33}H_{40}F_3O_5P_2S_3Rh$ : C, 47.5; H, 4.8%. Electronic spectrum  $\lambda_{max}$ : 282 ( $\epsilon$  9942  $M^{-1} cm^{-1}$ ), 328 ( $\epsilon$  7650  $M^{-1} cm^{-1}$ ), 368 (sh) nm.  $^1H$ -NMR ( $CDCl_3$   $\delta$ ): 0.92, 1.38 (each t, 7 Hz,  $OCH_2Me$ ); 1.50 (d,  $^4J(^{31}P-^1H)$  3.5 Hz,  $C_5Me_5$ ); 2.80, 4.09 (each dq, 7 Hz (q), 9.6, 8.6 Hz (d)  $OCH_2$ ); 7.41–7.53 (br,  $PPh_3$ ).  $^{31}P\{^1H\}$ -NMR ( $CDCl_3$   $\delta$ ): 37.3 (d,d,  $^1J(^{103}Rh-^{31}P)$  145 Hz;  $^3J(^{31}P-^{31}P)$  18 Hz;  $PPh_3$ ); 84.9 (d,d;  $^2J(^{103}Rh-^{31}P)$  12 Hz;  $^3J(^{31}P-^{31}P)$  18 Hz, dithio).

Complexes **3b** and **3c** were prepared similarly and the pertinent data are as follows:

#### 3.3.1. $[Cp^*Rh\{S_2P(OEt)_2\}(Ptol_3)][SO_3CF_3]$ (**3b**)

M.p. 198–199°C. Found: C, 49.2; H, 5.6. Anal. Calc.  $C_{36}H_{46}F_3O_5P_2S_3Rh$ : C, 49.3; H, 5.3%. Electronic spectrum:  $\lambda_{max}$  284 ( $\epsilon$  11578  $M^{-1} cm^{-1}$ ), 328 ( $\epsilon$  7843  $M^{-1} cm^{-1}$ ), 369 (sh) nm.  $^1H$ -NMR ( $CDCl_3$   $\delta$ ): 0.91, 1.37 (each t, 7 Hz,  $OCH_2Me$ ); 1.48 (d,  $^4J(^{31}P-^1H)$  3.5 Hz;

$C_5Me_5$ ); 2.38 (s,  $tolMe$ ); 2.77, 4.09 (each dq, 7 Hz (q); 9.3, 8.5 Hz (d);  $OCH_2$ ); 7.22–7.37 (m,  $C_6H_4$ ).  $^{31}P\{^1H\}$ -NMR ( $CDCl_3$   $\delta$ ): 35.8 (d,d  $^1J(^{103}Rh-^{31}P)$  145 Hz;  $^3J(^{31}P-^{31}P)$  18.5 Hz;  $PPh_3$ ); 84.9 (d,d,  $^2J(^{103}Rh-^{31}P)$  11 Hz;  $^3J(^{31}P-^{31}P)$  18.5 Hz, dithio).

#### 3.3.2. $[Cp^*Rh\{S_2P(OEt)_2\}(AsPh_3)][SO_3CF_3]$ (**3c**)

M.p. 162–163°C. Found: C, 44.3; H, 4.4. Anal. Calc.  $C_{33}H_{40}AsF_3O_5PS_3Rh$ : C, 45.1; H, 4.6%. Electronic spectrum  $\lambda_{max}$ : 284 ( $\epsilon$  9279  $M^{-1} cm^{-1}$ ), 321 ( $\epsilon$  6235  $M^{-1} cm^{-1}$ ), 393 nm ( $\epsilon$  4353  $M^{-1} cm^{-1}$ ).  $^1H$ -NMR in  $CDCl_3$   $\delta$ : 0.88, 1.38 (each t, 7 Hz,  $OCH_2Me$ ); 1.57 (s,  $C_5Me_5$ ); 2.72, 4.10 (dq) 7 Hz (t), 9 Hz (d),  $OCH_2$ ); 7.47–7.52 (br,  $AsPh_3$ ).  $^{31}P\{^1H\}$ -NMR ( $CDCl_3$   $\delta$ ): 83.3 (d,  $^2J(^{103}Rh-^{31}P)$  13 Hz, dithio).

### 3.4. Reaction between **2** and $[Cp^*Rh(\mu-Cl)Cl]_2$

To a dichloromethane solution (5 ml) of  $[Cp^*Rh\{S_2P(OEt)_2\}]$  (41 mg, 0.068 mmol), a solution of  $[Cp^*Rh(\mu-Cl)Cl]_2$  (21 mg, 0.034 mmol) in dichloromethane was added with stirring, which was continued for 30 min. The solvent was evaporated in vacuo to give **1a** in quantitative yield as characterized by microanalysis,  $^1H$ - and  $^{31}P$ -NMR data.

## 4. Crystallography

X-ray data on maroon crystals of  $[Cp^*RhCl\{S_2P(OEt)_2\}]$  (**1a**) were collected at 294 K on an Enraf–Nonius CAD-4 diffractometer using graphite monochromated  $Mo-K_\alpha$  radiation ( $\lambda = 0.71073$  Å) employing the  $\omega - 2\theta$  scan technique. The unit cell parameters were determined from 25 reflections measured by random search routine and indexed by the method of short vectors followed by least-squares refinement. The intensity data were corrected for Lorentz-polarization and absorption effects. The structure was solved using SHELXS 86 [27] and refined using SHELXL 93 [28] computer programs. The non-hydrogen atoms were refined anisotropically and are shown in Fig. 2. Crystallographic data together with data collection details are given in Table 2. Positional parameters are given in Table 3. An ORTEP drawing [29] of **1a** is shown in Fig. 2.

## Acknowledgements

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Table 2  
Crystal data and structure refinement details for [Cp\*RhCl{S<sub>2</sub>P(OEt)<sub>2</sub>}

Empirical formula	C <sub>14</sub> H <sub>25</sub> ClO <sub>2</sub> PS <sub>2</sub> Rh
Formula weight	458.8
Temperature	293(2) K
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /n
Unit cell dimensions	
<i>a</i> (Å)	12.731(2)
<i>b</i> (Å)	9.171(3)
<i>c</i> (Å)	17.437(8)
$\beta$ (°)	108.87(2)
<i>V</i> (Å <sup>3</sup> )	1926.5(12)
<i>Z</i>	4
<i>D</i> <sub>calc.</sub> (Mg m <sup>-3</sup> )	1.582
Absorption coefficient (mm <sup>-1</sup> )	1.325
<i>F</i> (000)	936
Crystal size	0.1 × 0.1 × 0.08 mm
Theta range of data collection (°)	2.39–24.97
Index ranges	0 ≤ <i>h</i> ≤ 15; 0 ≤ <i>k</i> ≤ 10; –20 ≤ <i>l</i> ≤ 19
Reflections collected	3547
Independent reflections	3385 [ <i>R</i> <sub>int</sub> = 0.0262]
Absorption correction	$\psi$ scan
Max and min transmission	0.97 and 0.72
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	3383/0/191
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.079
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0381, <i>wR</i> <sub>2</sub> = 0.0925
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0506; <i>wR</i> <sub>2</sub> = 0.1060
Largest difference peak and hole (eÅ <sup>-3</sup> )	0.684 and –0.565

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Table 3  
Atomic coordinates (×10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> × 10<sup>3</sup>) for [Cp\*RhCl{S<sub>2</sub>P(OEt)<sub>2</sub>}<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Rh	9879(1)	2253(1)	6784(1)	40(1)
Cl	10173(1)	4818(2)	6635(1)	65(1)
S(1)	10815(1)	2324(2)	8246(1)	59(1)
S(2)	8289(1)	2772(2)	7219(1)	52(1)
P	9350(1)	2858(2)	8340(1)	51(1)
O(1)	8983(4)	1952(6)	8968(2)	100(2)
O(2)	9361(3)	4367(5)	8778(2)	69(1)
C(1)	9716(6)	5(6)	6472(4)	72(2)
C(2)	10837(6)	503(10)	6559(4)	98(3)
C(3)	10712(6)	1600(8)	5964(5)	84(2)
C(4)	9621(6)	1746(7)	5532(3)	68(2)
C(5)	9024(5)	800(6)	5813(3)	59(1)
C(6)	9348(13)	–1164(8)	6921(7)	178(6)
C(7)	11893(10)	–73(17)	7157(7)	264(11)
C(8)	11697(11)	2408(15)	5844(10)	249(10)
C(9)	9169(12)	2759(10)	4818(5)	160(5)
C(10)	7769(6)	636(11)	5469(6)	137(4)
C(11)	8461(10)	729(10)	8868(5)	141(4)
C(12)	8178(6)	114(8)	9536(4)	88(2)
C(13)	9665(7)	5701(7)	8461(4)	89(2)
C(14)	10056(7)	6764(8)	9091(4)	96(2)

<sup>a</sup> *U*<sub>eq</sub> is defined as one third of the trace of the orthogonalized *U*<sub>*ij*</sub> tensor.

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