Preparation and Structural Studies of Diphenylthiophosphinito Rhodium(III) Complexes. *X*-Ray Structure Analysis of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}Cl)_2(\mu\text{-}Ph_2PS)][BPh_4]$†

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The tri-μ-hydroxo-dirhodium complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)_3][ClO_4]$ (**1**) reacts with the appropriate amount of $Ph_2P(S)H$, in acetone, to give $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)_n(\mu\text{-}Ph_2PS)_{3-n}][ClO_4]$ [n = 0(**2**) or 1(**3**)]. Reaction of complex (**1**) with an equimolar amount of $Ph_2P(S)H$, in methanol gave the di-μ-methoxo-μ-diphenylthiophosphinito complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OMe)_2(\mu\text{-}Ph_2PS)][ClO_4]$ (**5**). The mixed-bridged complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OMe)(\mu\text{-}pz)(\mu\text{-}Ph_2PS)][ClO_4]$ (**6**) (pz = pyrazolate) was obtained by addition of $Ph_2P(S)H$ to a methanolic solution of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)(\mu\text{-}pz)_2][ClO_4]$. The complexes (**5**) and $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)(\mu\text{-}Ph_2PS)_2][ClO_4]$ (**3**) react with HCl yielding the binuclear chloride compounds $[\{(C_5Me_5)Rh\}_2(\mu\text{-}Cl)_2(\mu\text{-}Ph_2PS)][ClO_4]$ (**7**) and $[\{(C_5Me_5)Rh\}_2(\mu\text{-}Cl)(\mu\text{-}Ph_2PS)_2][ClO_4]$ (**9**). The doubly homo-bridged complex $[\{(C_5Me_5)Rh(Bu^tNC)\}_2(\mu\text{-}Ph_2PS)_2][ClO_4]_2$ (**10**) can be prepared from $[(C_5Me_5)Rh(acac)(Bu^tNC)][ClO_4]$ (acac = acetylacetonate ion) and an equimolar amount of $Ph_2P(S)H$. The mononuclear species $[(C_5Me_5)Rh(acac)Cl]$ reacts with an equimolar amount of $Ph_2P(S)H$ in the presence of $NaBPh_4$ giving the binuclear complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}Cl)(\mu\text{-}Ph_2PS)_2][BPh_4]$ (**11**). Its n.m.r. spectra show the presence of two isomers. Reaction of $[\{(C_5Me_5)RhCl\}_2(\mu\text{-}Cl)_2]$ with $Ph_2P(S)H$ and KOH yields the mononuclear complex $[(C_5Me_5)Rh(Ph_2PS\text{-}P)(Ph_2PS\text{-}PS)]$ (**12**). This compound is converted by sulphur-atom abstraction into $[(C_5Me_5)Rh(Ph_2PS\text{-}P)(Ph_2PS_2\text{-}SS)]$ (**13**). The *X*-ray structure analysis of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}Cl)_2(\mu\text{-}Ph_2PS)][BPh_4]$ (**8**) is also reported: the crystals are triclinic, space group $P\bar{1}$, and have been refined to R 0.035 and R' 0.038. The rhodium–rhodium distance is 3.570 1(5) Å.

The co-ordination chemistry of metallic derivatives of the pyrazolate ligand has been investigated.[1] In particular, the use of pyrazolate type ligands has proved to be important for the isolation of some unusual methoxo-, hydroxo-, and pyrazolato-bridged pentamethylcyclopentadienyl rhodium complexes.[2]

Deprotonated diphenylphosphine sulphide (Ph_2PS^-) is an anionic ligand which, like the pyrazolate anion, has two directly bonded donor centres. A variety of platinum metal complexes containing the Ph_2PS^- ligand, either *S*-bonded,[3,4] *P*-bonded,[5,6] or *S*- and *P*-bonded (bridge[7–9] or side-on[4,10]) have been described in recent years.

In the present paper we describe a study of the co-ordination properties of the Ph_2PS^- anion towards $(C_5Me_5)Rh$ moieties. Part of this work has been reported in a preliminary communication.[11]

Results and Discussion

The tri-μ-hydroxo complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)_3][ClO_4]$ (**1**) reacted with $Ph_2P(S)H$ (mole ratio 1:3 or excess), in acetone, to give the triply bridged complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}Ph_2PS)_3][ClO_4]$ (**2**). The i.r. spectrum of (**2**) showed a ν(P–S) band at 570 cm^{-1}, and the ^1H n.m.r. spectrum consisted of two C_5Me_5 peaks at δ 1.11(t) and 1.24(d), of equal intensity, indicative of the presence of two different environments for the rhodium atoms. This dirhodium(III) compound is relatively similar to a reported phosphito complex of formula $[\{(C_5Me_5)Rh\}_2\{\mu\text{-}(MeO)_2PO\}_3]^+$ prepared by Kläui *et al.*[12] In this context, it is interesting that all attempts to prepare the triply bridged complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)_3]^+$ using the pyrazolate (pz) ligand have been unsuccessful, and only neutral doubly bridged complexes $[\{(C_5Me_5)Rh(pz)\}_2(\mu\text{-}pz)_2]$ were obtained when using excess of pyrazolate.[2b]

When the above mentioned reaction between complex (**1**) and $Ph_2P(S)H$ was performed using a 1:2 mole ratio the hetero-bridged complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)(\mu\text{-}Ph_2PS)_2][ClO_4]$ (**3**) was obtained, which shows only one C_5Me_5 peak in its ^1H n.m.r. spectrum at δ 1.28(d) [J(PH) 3.5 Hz]. Furthermore we have attempted the synthesis of the intermediate $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)_2(\mu\text{-}Ph_2PS)][ClO_4]$ (**4**) by treating (**1**) with $Ph_2P(S)H$ in 1:1 mole ratio; the ^1H n.m.r. spectrum of the resulting mixture showed the presence of unreacted (**1**), (**3**), and the proposed complex (**4**) [δ(C_5Me_5) 1.39(d) and 1.66(s), J(PH) 3.1 Hz], which however was not isolated in the solid state. These observations suggest that the rate of formation of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)_2(\mu\text{-}Ph_2PS)]^+$ (**4**) from $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)_3]^+$ is slower than that of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)(\mu\text{-}Ph_2PS)_2]^+$ (**3**) from (**4**), as recently proposed for the similar $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)_{3-n}(\mu\text{-}pz)_n]^+$ (n = 1 or 2) complexes.[2a]

Interestingly when the reaction between (**1**) and $Ph_2P(S)H$ (1:1 mole ratio) was performed in methanol the hetero-bridged complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OMe)_2(\mu\text{-}Ph_2PS)][ClO_4]$ (**5**) was isolated. Its ^1H n.m.r. spectrum showed the presence of two C_5Me_5 peaks at δ 1.48(d) [J(PH) 3.0 Hz] and 1.65(s), and one OMe peak at δ 3.50(s). These data suggest that the cations contain one bridging thiophosphinito and two bridging

† Di-μ-chloro-μ-diphenylthiophosphinito-*PS*-bis[(η-pentamethylcyclopentadienyl)rhodium(III)] tetraphenylborate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

methoxo groups. Presumably all these reactions occur *via* protonation of the hydroxo or methoxo bridges of the starting complexes (the $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OMe)_3]^+$ intermediate should be formed by reaction of (**1**) with methanol) by the $Ph_2P(S)H$ ligands to form aqua or methanol intermediates which react with thiophosphinito groups (Ph_2PS^-) to give the reported complexes (**2**)—(**5**). Noteworthy is the close parallelism between the Ph_2PS^- and pz^- ligands towards the formation of the hetero-bridged complexes $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OR)_{3-n}(\mu\text{-}L)_n]^+$ (R = Me, n = 1; R = H, n = 1 or 2; L = Ph_2PS or pz). However, the synthesis of complex (**2**) is a unique feature of the Ph_2PS^- ligand.

The mixed-bridged complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OMe)(\mu\text{-}pz)(\mu\text{-}Ph_2PS)][ClO_4]$ (**6**) can be prepared by treating $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)(\mu\text{-}pz)_2][ClO_4]$ with $Ph_2P(S)H$ (1:1 mole ratio) in methanol [$\delta(C_5Me_5)$: 1.32(d), J(PH) 3.50; 1.61(s); $\delta(OCH_3)$ 3.50(d), J(PH) 1.29; δ(pz) 6.52(t) and 8.07(d), J(HH) = 2.0 Hz]. Attempts to prepare μ-hydrido complexes by adding $Ph_2P(S)H$ (mole ratio 1:1) to a solution of (**1**) in propan-2-ol have been unsuccessful, although the μ-hydrido-μ-pyrazolate complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}H)_2(\mu\text{-}pz)][BF_4]$ has been obtained from $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)_3][BF_4]\cdot H_2O$ with pyrazole in propan-2-ol.[13]

When an acetone solution of the di-μ-methoxo-μ-thiophosphinato-rhodium(III) complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OMe)_2(\mu\text{-}Ph_2PS)][ClO_4]$ (**5**) was treated with 2 equivalents of HCl it quantitatively yielded the triply-bridged complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}Cl)_2(\mu\text{-}Ph_2PS)][ClO_4]$ (**7**) plus 2 mol of methanol. The ^{1}H n.m.r. spectrum of (**7**) shows a singlet at δ 1.68 and one doublet at 1.34 [J(PH) 3.3 Hz] arising from two different types of C_5Me_5 environment. Since the red crystals of (**7**) deteriorated rapidly when removed from the solution, the BPh_4 analogue (**8**) was prepared, which showed satisfactory crystal stability, so enabling an *X*-ray crystallographic study to be made (discussed below).

The chloro-bridged complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}Cl)(\mu\text{-}Ph_2PS)_2][ClO_4]$ (**9**) was isolated from the reaction of complex (**3**) with 1 equivalent of HCl in acetone. Both the above reactions imply preferential protonation of the methoxo or hydroxo groups and the displacement of the neutral methanol or water formed, by μ-chlorides. The products (**7**) and (**9**) are directly related to recently reported pyrazolate complexes $[\{(C_5Me_5)Rh\}_2(\mu\text{-}Cl)_2(\mu\text{-}pz)][BF_4]$ and $[\{(C_5Me_5)Rh\}_2(\mu\text{-}Cl)(\mu\text{-}pz)_2][BF_4]$ also prepared in our laboratory.[13]

A doubly homo-bridged complex $[\{(C_5Me_5)Rh(Bu^tNC)\}_2(\mu\text{-}Ph_2PS)_2][ClO_4]_2$ (**10**) can readily be prepared by treating $[(C_5Me_5)Rh(acac)(Bu^tNC)][ClO_4]$ (acac = acetylacetonate ion) with $Ph_2P(S)H$ (mole ratio 1:1) in acetone. The i.r. spectrum of complex (**10**) showed the presence of only one broad ν(CN) band at 2 180 cm^{-1}, whilst its ^{1}H n.m.r. spectrum showed two resonances in the ratio 30:18, a doublet at δ 1.80 [30 H, J(PH) 2.4 Hz] and a singlet at 1.16 (18 H). These spectral data are fully in accord with the Bu^tNC ligand occupying a terminal position. Other diketonato complexes such as $[(C_5Me_5)Rh(acac)L][ClO_4]$ [L = pyridine (py) or PPh_3] also reacted with $Ph_2P(S)H$ in acetone, but an unidentified mixture of products was formed. When $[(C_5Me_5)Rh(acac)Cl]$ was treated with $Ph_2P(S)H$ in the presence of $NaBPh_4$ in methanol the hetero-bridged complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}Cl)(\mu\text{-}Ph_2PS)_2][BPh_4]$ (**11**) was obtained. In solution this appears to be a mixture of an asymmetric (**11a**) and a symmetric (**11b**) isomer. In (**11a**) the Ph_2PS unit forms Rh–P–S–Rh bridges in such a fashion as to generate a '$(C_5Me_5)RhP_2$' and a '$(C_5Me_5)RhS_2$' unit. Accordingly, in the ^{1}H n.m.r. spectrum the asymmetry of the complex (**11a**) was indicated by two C_5Me_5 peaks with a singlet at δ 1.58 and a triplet at 1.17 [J(PH) 4.0 Hz]. In (**11b**) each $(C_5Me_5)Rh$ unit is co-ordinated to one P and one S donor atom so that the ^{1}H n.m.r. spectrum shows only one C_5Me_5 peak at δ 1.16(d) [J(PH) 3.4 Hz]. Interestingly, when the reaction between $[(C_5Me_5)Rh(acac)Cl]$ and $Ph_2P(S)H$ was performed in acetone only the symmetric isomer (**11b**) was obtained. These compounds are similar to recently reported complexes of formula $[\{(C_5H_5)Ni\}_2(\mu\text{-}R_2PS)_2]$ prepared recently by Kläui *et al.*[14] The rate of isomerization of compounds (**11a**) and (**11b**) is solvent dependent, whereas Kläui demonstrated that isomerization of the nickel complexes was an intramolecular process without involvement of monomeric units.

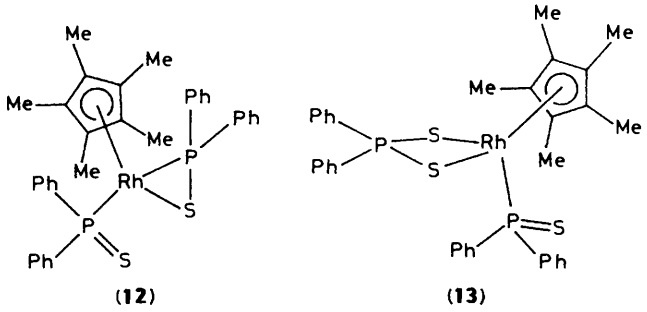

Figure 1. Proposed structure for complex (**12**) and structural diagram of complex (**13**)

The complexes discussed so far in this study show the Ph_2PS ligand in a bridging mode between the two metal centres. However as stated earlier, side- or end-on co-ordination is also possible.

Reaction of $[\{(C_5Me_5)RhCl\}_2(\mu\text{-}Cl)_2]$ with a mixture of $Ph_2P(S)H$ and potassium hydroxide in methanol, at room temperature, led to the formation of $[(C_5Me_5)Rh(Ph_2PS\text{-}P)(Ph_2PS\text{-}PS)]$ (**12**) as an orange solid. In its ^{1}H n.m.r. spectrum, coupling between the hydrogen atoms of the C_5Me_5 ring and phosphorus was detected [J(PH) 3.2 Hz], giving a pseudo-triplets at δ 1.42 for this resonance. Such coupling is consistent with direct rhodium–phosphorus bonds, a fact further supported by the ^{31}P n.m.r. data, which shows the presence of two inequivalent phosphorus nuclei each giving a doublet of doublets centred at 54.8 (P^1) and 49.8 (P^2) p.p.m. respectively [$^1J(RhP^1)$ 142, $^1J(RhP^2)$ 120, $^2J(P^1P^2)$ 35 Hz]. In particular, the small value of $^1J(RhP^2)$ and the requirement of six-co-ordination for the Rh^{III} centre suggest the incorporation of P^2 into a three-membered ring system. These spectroscopic data, together with the molecular weight determination for complex (**12**) support the presence of two different Ph_2PS ligands; one co-ordinated 'end-on' through phosphorus, the other 'side-on' through phosphorus and sulphur to the same metal centre (Figure 1).

When a solution of (**12**) in methanol was left to stand for 24 h, the complex was slowly converted into the dithiophosphinate compound (**13**). On the basis of the ^{1}H n.m.r. [(C_5Me_5) 1.32(d), J(PH) 3.4 Hz] and the ^{31}P n.m.r. data [$\delta(P^1)$ 63.2, $^1J(RhP^1)$ 128, $^3J(P^1P^2)$ 11; $\delta(P^2)$ 83.0 p.p.m., $^2J(RhP^2) = {}^3J(P^1P^2)$ 11 Hz], as well as the i.r. data [$\nu(PS_2)$ 590, 575; ν(PS) 630 cm^{-1}] and elemental analyses, complex (**13**) was formulated as $[(C_5Me_5)Rh(Ph_2PS\text{-}P)(Ph_2PS_2\text{-}SS)]$ (Figure 1). These spectroscopic data are also in accord with those found by Robertson and Stephenson[15] for a rhodium(III) complex containing the Ph_2PS_2 ligand.

The formation of the dithio-complex (**13**) from (**12**) presumably occurs *via* an intermolecular process that may be seen as a nucleophilic attack on the endocyclic electrophile of the *PS*-co-ordinated Ph_2PS, by the sulphur atom of a second molecule. Consequently, the highly reactive three-membered ring $\overline{RhP(Ph)_2S}$ formed in (**12**) undergoes sulphur insertion reaction and the stable four-membered $\overline{RhSP(Ph)_2S}$ ring struc-

Table 1. Analytical, i.r. data, colour, and yields for the new complexes

	Complex	Analysis[a]/% C	H	N	I.r.[b]/cm^{-1}	Colour	Yield /%
(2)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}Ph_2PS)_3][ClO_4]$	54.2 (54.6)	4.5 (4.9)		570vs[c]	Red	85
(3)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)(\mu\text{-}Ph_2PS)_2][ClO_4]$	51.4 (51.4)	5.0 (5.0)		3 540w[d], 570[c]	Orange	80
(5)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}OMe)_2(\mu\text{-}Ph_2PS)][ClO_4]$	47.8 (47.7)	5.0 (5.4)		550vs,[c] 520vs,[e] 1 050s[f]	Orange	76
(6)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}OMe)(\mu\text{-}pz)(\mu\text{-}Ph_2PS)][ClO_4]$	48.5 (48.5)	5.2 (5.2)	3.9 (3.1)	550vs,[c] 530vs,[e] 1 050s[f]	Green	75
(7)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}Cl)_2(\mu\text{-}Ph_2PS)][ClO_4]$	44.2 (44.4)	5.2 (5.6)		555vs,[c] 275w[g]	Red	65
(8)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}Cl)_2(\mu\text{-}Ph_2PS)][BPh_4]$	62.7 (62.0)	5.5 (5.5)		555,[c] 275w[g]	Red	80
(9)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}Cl)(\mu\text{-}Ph_2PS)_2][ClO_4]$	50.4 (50.5)	3.9 (3.8)		565vs,[c] 275s[g]	Red	75
(10)	$[\{(C_5Me_5)Rh(Bu^tNC)\}_2(\mu\text{-}Ph_2PS)_2][ClO_4]_2$	50.9 (50.8)	5.9 (5.4)	2.3 (2.2)	2 180vs,[h] 580vs[c]	Orange	90
(11)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}Cl)(\mu\text{-}Ph_2PS)_2][BPh_4]$	64.5 (64.5)	5.6 (5.5)		550vs,[c] 250w[g]	Red	80
(12)	$[(C_5Me_5)Rh(Ph_2PS\text{-}P)(Ph_2PS\text{-}PS)]$	59.9 (60.6)	5.3 (5.2)		525s,[c] 590vs[c]	Red	40
(13)	$[(C_5Me_5)Rh(Ph_2PS\text{-}P)(Ph_2PS_2\text{-}SS)]$	57.8 (57.9)	4.9 (5.0)		590vs,[i] 575vs,[i] 630vs[c]	Red	50

[a] Calculated values are given in parentheses. [b] Nujol mulls. [c] ν(P–S). [d] ν(O–H). [e] ν(Rh–O). [f] ν(C–O). [g] ν(Rh–Cl). [h] ν(C–N). [i] ν(PS_2).

Table 2. Proton and $^{31}P\text{-}\{^1H\}$ n.m.r. data[a] for the new complexes

Complex	^1H δ(C_5Me_5)	^4J(PH)	$^{31}P\text{-}\{^1H\}$ δ(P)	^1J(RhP)	^3J(PP)	Others
(2)[b]	1.11(t)	3.5	52.3(dd)	138	7	
	1.24(d)	3.2	61.4(dt)	141	7	
(3)[b]	1.28(d)	3.5	79.5(d)	144		
(5)[b]	1.48(d)	3.0	72.8(d)	161		3.50(s)[c]
	1.65(s)					
(6)[b]	1.32(d)	3.5	124.8(d)	168		6.52(t),[d] 8.07(d)[d]
	1.61(s)					3.50(d)[c]
(7)[e]	1.34(d)	3.3	63.9(d)	135		
	1.68(s)					
(10)[e]	1.80(d)	2.4	59.2(d)	98		1.16(s)[f]
(11a)[b]	1.17(t)	4.0	73.7(d)	136		
	1.58(s)					
(11b)[b]	1.16(d)	3.4	78.0(d)	137		
(12)[b]	1.42(pt)	3.2	49.8(dd)	120	35[g]	
			54.8(dd)	142	35[g]	
(13)[b]	1.32(d)	3.4	63.2(dd)	128	11	
			83.0(pt)	11	11	

[a] Chemical shift (p.p.m.) relative to $SiMe_4$ (multiplicity). Coupling constants are in Hz. [b] In $CDCl_3$. [c] OCH_3 protons. [d] Pyrazolate protons. [e] In $(CD_3)_2CO$. [f] Bu^tNC protons. [g] ^2J(PP).

ture is formed. The structure of complex (**13**) has been determined by *X*-ray methods.[11]

These results confirm, alongside previous work on rhodium chemistry for different formal oxidation states[(II) or (III)], the remarkable ability of the thiophosphinito ligand to stabilize a variety of doubly [$Rh(\mu\text{-}Ph_2PS)_2Rh$ (**10**)] and triply bridged species ['$Rh(\mu\text{-}Ph_2PS)_{3-n}(\mu\text{-}Y)_nRh$' ($n$ = 1 or 2, Y = OH (**3**), (**4**), or Cl (**7**), (**8**), (**9**), (**11**); n = 2, Y = OMe (**5**); n = 0 (**2**)]. Finally, it is worth noting that 'end-on' and 'side-on' co-ordination modes for the thiophosphinito ligand have been found in complexes (**12**) and (**13**). Analytical, selected i.r. data, and yields for all the new complexes prepared are collected in Table 1 and ^1H and ^{31}P n.m.r. data are given in Table 2.

Description of the Structure of Complex (**8**).—The compound $[C_{32}H_{40}Cl_2PRh_2S]^+[BPh_4]^-$ (**8**) is a binuclear complex (Figure 2)[16] with both rhodium atoms co-ordinating octahedrally assuming each C_5Me_5 ring can be regarded as occupying three facial sites.

The Rh(1)···Rh(2) separation of 3.5701(5) Å (Table 3) is significantly longer than for the rhodium–rhodium distance [3.397(1) Å] in the directly analogous pyridazine complex.[17] The chlorine atoms are in a 'folded' geometry,[18] with the dihedral angle between the planes through Rh(1), Cl(1), Cl(2) and Rh(2), Cl(1), Cl(2) being equal to 30.57(4)° *cf.* 37.00(6)° for the dichloro pyridazine complex.[17] Due to the flexibility of the (Rh, Cl, Cl, Rh) group[18] the arrangement adopted, as far as the Rh–Cl distance is concerned, is likely to reflect steric factors.

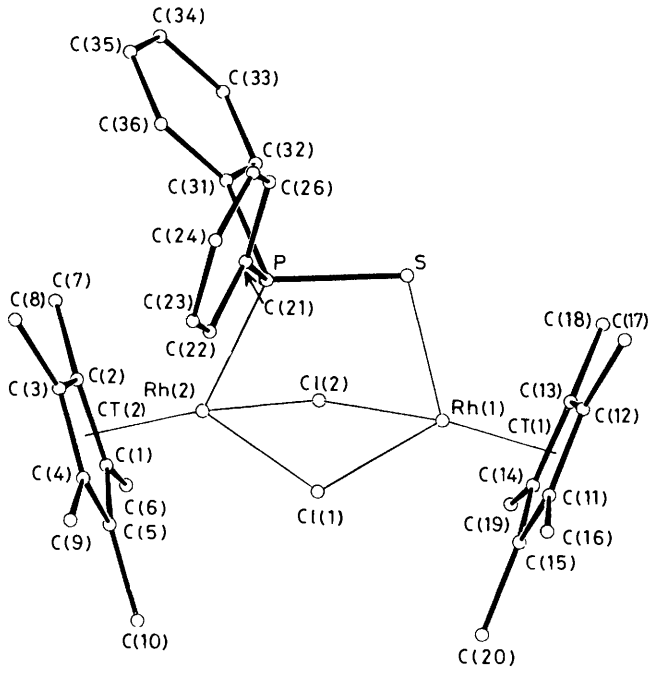

Figure 2. ORTEP drawing of complex (**8**) showing the atomic numbering

Table 3. Selected geometrical parameters for $[\{(C_5Me_5)Rh\}_2(\mu\text{-}Cl)_2(\mu\text{-}Ph_2PS)][BPh_4]$ (**8**)

(*a*) Bond distances (Å) and angles (°)

Rh(1)–Rh(2)	3.570 1(5)	Rh(2)–Cl(2)	2.587(1)
Rh(1)–Cl(1)	2.631(1)	Rh(2)–P	2.345(1)
Rh(1)–Cl(2)	2.458(1)	Rh(2)–CT(2)*	1.810(2)
Rh(1)–S	2.393(1)	C(21)–P	1.919(5)
Rh(1)–CT(1)*	1.781(2)	C(31)–P	1.856(5)
Rh(2)–Cl(1)	2.466(1)	P–S	2.093(2)
S–Rh(1)–CT(1)	128.00(8)	Cl(2)–Rh(2)–CT(2)	123.21(9)
S–Rh(1)–Cl(1)	89.90(4)	Rh(1)–Cl(1)–Rh(2)	89.30(4)
S–Rh(1)–Cl(2)	87.66(4)	Rh(1)–Cl(2)–Rh(2)	90.06(4)
Cl(1)–Rh(1)–Cl(2)	85.47(4)	Rh(1)–S–P	104.1(1)
Cl(1)–Rh(1)–CT(1)	125.61(8)	Rh(2)–P–S	112.0(1)
Cl(2)–Rh(1)–CT(1)	126.94(8)	C(21)–P–C(31)	107.9(2)
P–Rh(2)–CT(1)	133.38(8)	Rh(2)–P–C(21)	114.0(2)
P–Rh(2)–Cl(1)	86.43(4)	C(21)–P–S	107.7(2)
P–Rh(2)–Cl(2)	86.99(4)	C(31)–P–S	103.5(2)
Cl(1)–Rh(2)–Cl(2)	86.67(4)	Rh(2)–P–C(31)	111.2(1)
Cl(1)–Rh(2)–CT(1)	125.78(9)		

(*b*) Some least-square planes; deviations (Å) of some atoms in parentheses

(i) Rh(1), Cl(1), Rh(2)
(ii) Rh(1), Cl(2), Rh(2)
(iii) P, S, Rh(1), Rh(2)
(iv) P, S, Rh(2) [C(21) −1.479(5), C(31) 1.565(5)]
(v) P, C(21), C(31) [S −1.860 9(11), Rh(2) 1.776 4(5)]
(vi) C(1), C(2), C(3), C(4), C(5)
(vii) C(11), C(12), C(13), C(14), C(15)

Planes	Angles (°)
(i)—(ii)	148.5(1)
(i)—(iii)	106.3(1)
(ii)—(iii)	105.2(1)
(iii)—(v)	89.7(1)
(iv)—(v)	89.0(1)
(vi)—(vii)	41.9(2)

* CT(1) and CT(2) are the centroids of the pentamethylcyclopentadienyl rings.

The position of the diphenylthiophosphinito ligand with respect to the central part of the complex can be described by the angle between the planes through P, C(21), C(31) and P, S, Rh(1), Rh(2), equal to 89.7(1)°. The pentamethylcyclopentadienyl rings, C(1)—C(5) and C(11)—C(15), are located almost symmetrically with respect to the four-membered ring, making angles of 97.1(1) and 96.4(1)° respectively with it. The angle between the two C_5Me_5 rings is 41.9(2)°, *cf.* 37.9(5)° in above mentioned dichloro pyridazine complex,[17] and they are eclipsed [−1.0(4)°] with respect to each other.

The Rh(1)–S distance [2.393(1) Å] is in the range of rhodium–sulphur distances for similar complexes, 2.372(2)—2.403(2) Å.[11,19] The co-ordination distance Rh(2)–P [2.345(1) Å] is longer than those reported for a complex of diphenylphosphine,[20] but compares well with that reported[11] for $[(C_5Me_5)Rh(Ph_2PS\text{-}P)(Ph_2PS_2\text{-}SS)]$ of 2.335(2) Å. The C(21)–P–C(31) angle [107.9(2)] is smaller than Rh(2)–P–S [112.0(1)°]. The P–S distance [2.093(2)Å] is within the range of distances for the complex in ref. 11.

The methyl groups of the C_5Me_5 rings point away from the rhodium atoms [range of deviation: 0.015(7)—0.209(6) Å and 0.003(6)—0.102(7) Å, for each of the rings]. In the C(1)—C(5) ring there are some short contacts with the phenyl groups: H(8b)···H(22) 2.6(1), H(8a)···H(36) 2.5(1), and H(9c)···H(22) 2.9(1) Å.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer (range 4 000—200 cm^{-1}) using Nujol mulls between polyethylene sheets. The C, H, and N analyses were carried out with a Perkin-Elmer 240B microanalyser. N.m.r. spectra were recorded in $CDCl_3$ or $(CD_3)_2CO$ solutions at room temperature on a Varian XL200 Spectrometer. Proton n.m.r. shifts are reported with respect to $SiMe_4$, $^{31}P\text{-}\{^1H\}$ n.m.r. shifts to external 85% H_3PO_4. All reactions were carried out at room temperature unless stated otherwise. Solvents were dried and distilled before use.

Starting materials were prepared according to literature procedures: $[\{(C_5Me_5)Rh\}(\mu\text{-}OH)_3][ClO_4]$,[21] $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)(\mu\text{-}pz)_2][ClO_4]$,[2a] $[(C_5Me_5)RhCl(acac)]$,[22] $[(C_5Me_5)Rh(acac)(Bu^tNC)][ClO_4]$,[22] and $[\{(C_5Me_5)RhCl\}_2(\mu\text{-}Cl)_2]$.[23] Other chemicals were reagent grade products and were used without further purification.

Preparations.—Complexes (**2**) *and* (**3**) *from* (**1**). Solid $Ph_2P(S)H$ (104.5 mg, 0.48 mmol) was added to a solution of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)_3][ClO_4]$ (100 mg, 0.16 mmol) in acetone (20 cm^3). The yellow solution rapidly turned red. After stirring for 20 min the volume of the solution was reduced to *ca.* 3 cm^3, and addition of diethyl ether led to precipitation of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}Ph_2PS)_3][ClO_4]$ (**2**). The red solid was filtered off, washed with diethyl ether, and air-dried.

Complex (**3**) was similarly prepared by the route described above, starting from the stoichieometric amount of $Ph_2P(S)H$.

Complex (**5**) *from* (**1**). To a solution of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)_3][ClO_4]$ (60 mg, 0.095 mmol) in deoxygenated methanol (10 cm^3) was added $Ph_2P(S)H$ (20.9 mg, 0.095 mmol) under a nitrogen atmosphere. The resulting orange suspension was stirred for 20 min, then the solvent was evaporated under reduced pressure to *ca.* 2 cm^3, and addition of diethyl ether led to complete precipitation of the orange complex (**5**). This was filtered off, washed with diethyl ether, and vacuum-dried.

Complex (**6**) *from* $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)(\mu\text{-}pz)_2][ClO_4]$. Addition of $Ph_2P(S)H$ (18.0 mg, 0.082 mmol) to a solution of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)(\mu\text{-}pz)_2][ClO_4]$ (60 mg, 0.082 mmol) in deoxygenated methanol (10 cm^3) caused a colour change from yellow to dark green. The solution was stirred for 5 h, under a nitrogen atmosphere. Then the solvent was evaporated under

Table 4. Final atomic co-ordinates for complex (**8**)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Rh(1)	0.186 30(2)	0.066 67(2)	0.226 74(3)	C(31)	0.120 2(2)	0.358 7(3)	0.168 6(5)
Rh(2)	0.272 70(2)	0.253 38(2)	0.087 37(3)	C(32)	0.132 6(3)	0.363 0(4)	0.319 4(5)
P	0.142 23(6)	0.261 39(7)	0.074 00(11)	C(33)	0.120 5(4)	0.436 6(4)	0.397 8(7)
S	0.088 97(6)	0.159 54(7)	0.169 86(13)	C(34)	0.096 2(5)	0.506 9(4)	0.325 5(8)
Cl(1)	0.242 52(7)	0.104 18(7)	0.000 59(11)	C(35)	0.084 0(4)	0.503 6(4)	0.177 0(8)
Cl(2)	0.266 12(6)	0.194 49(7)	0.327 03(11)	C(36)	0.096 2(3)	0.430 8(3)	0.096 5(6)
C(1)	0.384 5(3)	0.318 5(3)	0.166 7(6)	B	−0.321 2(3)	0.285 9(4)	0.397 8(5)
C(2)	0.329 8(3)	0.379 7(3)	0.126 5(6)	C(41)	−0.237 7(3)	0.294 5(3)	0.341 0(4)
C(3)	0.305 0(3)	0.369 3(3)	−0.025 5(6)	C(42)	−0.204 1(3)	0.372 6(4)	0.302 1(6)
C(4)	0.340 0(3)	0.297 0(3)	−0.078 5(5)	C(43)	−0.132 0(4)	0.382 3(6)	0.261 1(8)
C(5)	0.390 1(3)	0.268 6(3)	0.039 9(6)	C(44)	−0.091 5(4)	0.311 7(7)	0.255 6(6)
C(6)	0.426 1(3)	0.311 5(5)	0.313 8(7)	C(45)	−0.121 7(3)	0.234 0(5)	0.292 3(6)
C(7)	0.313 7(4)	0.450 0(4)	0.228 7(7)	C(46)	−0.193 2(3)	0.225 3(4)	0.334 1(6)
C(8)	0.257 7(4)	0.428 2(4)	−0.110 1(7)	C(51)	−0.368 0(3)	0.366 2(3)	0.334 2(5)
C(9)	0.334 4(4)	0.265 5(5)	−0.234 4(7)	C(52)	−0.401 5(3)	0.364 7(3)	0.191 7(5)
C(10)	0.439 6(3)	0.195 8(4)	0.029 9(8)	C(53)	−0.439 7(4)	0.432 2(4)	0.133 7(6)
C(11)	0.165 4(3)	−0.067 4(3)	0.172 3(5)	C(54)	−0.446 6(4)	0.503 8(4)	0.218 1(7)
C(12)	0.110 0(3)	−0.041 4(3)	0.257 0(5)	C(55)	−0.414 1(5)	0.507 7(4)	0.359 1(7)
C(13)	0.148 1(3)	−0.008 1(3)	0.393 9(5)	C(56)	−0.375 6(4)	0.440 0(4)	0.414 4(5)
C(14)	0.227 4(3)	−0.017 1(3)	0.396 2(5)	C(61)	−0.309 7(3)	0.293 2(3)	0.578 9(5)
C(15)	0.238 2(3)	−0.053 5(3)	0.258 4(5)	C(62)	−0.370 4(3)	0.303 4(4)	0.660 9(5)
C(16)	0.150 8(4)	−0.105 0(4)	0.019 5(6)	C(63)	−0.361 8(4)	0.311 7(4)	0.811 2(6)
C(17)	0.026 3(3)	−0.048 4(4)	0.212 9(7)	C(64)	−0.291 7(4)	0.312 7(4)	0.890 1(5)
C(18)	0.111 0(4)	0.020 9(5)	0.521 9(7)	C(65)	−0.231 4(4)	0.303 6(4)	0.814 7(5)
C(19)	0.286 7(4)	0.009 4(4)	0.520 0(6)	C(66)	−0.241 0(3)	0.293 4(4)	0.663 4(5)
C(20)	0.312 1(3)	−0.073 9(4)	0.214 3(7)	C(71)	−0.369 6(3)	0.193 9(3)	0.338 3(5)
C(21)	0.092 5(3)	0.262 7(3)	−0.108 3(5)	C(72)	−0.426 1(3)	0.152 4(3)	0.410 2(5)
C(22)	0.129 1(3)	0.242 0(4)	−0.227 6(6)	C(73)	−0.469 2(3)	0.077 5(4)	0.354 7(6)
C(23)	0.092 3(5)	0.241 1(5)	−0.368 0(7)	C(74)	−0.457 2(3)	0.039 1(4)	0.225 8(7)
C(24)	0.018 3(6)	0.259 5(5)	−0.388 5(8)	C(75)	−0.402 6(3)	0.076 5(4)	0.149 7(6)
C(25)	−0.018 5(4)	0.277 4(4)	−0.273 4(9)	C(76)	−0.360 1(3)	0.153 1(4)	0.205 0(5)
C(26)	0.017 5(3)	0.279 4(4)	−0.131 5(7)				

reduced pressure to *ca.* 2 cm^3, and addition of diethyl ether led to the precipitation of (**6**) as a dark green solid. This was filtered off, washed with diethyl ether, and vacuum-dried.

Complex (**7**) *from* (**5**). Hydrochloric acid (1.4 cm^3, 0.118 mol dm^{-3}, 0.162 mmol) in water was added to a solution of (**5**) (70 mg, 0.081 mmol) in deoxygenated acetone (10 cm^3). The resulting solution was stirred for 20 min under a nitrogen atmosphere. Vacuum evaporation to *ca.* 2 cm^3 and addition of diethyl ether led to precipitation of the red complex, which was filtered off, washed with diethyl ether, and vacuum-dried.

The orange μ-chloro complex (**9**) was similarly prepared by treating (**3**) (100 mg, 0.097 mmol) with HCl (0.83 cm^3, 0.118 mol dm^{-3}, 0.097 mmol).

Complex (**8**) *from* (**7**). To a solution of complex (**7**) (100 mg, 0.115 mmol) in methanol (20 cm^3) was added $NaBPh_4$ (39.6 mg, 0.115 mmol), and a red solid precipitated spontaneously. The resulting suspension was stirred for 20 min. The solid was filtered off, washed with methanol, and air-dried.

Complex (**10**). A mixture of $[(C_5Me_5)Rh(acac)(Bu^tNC)][ClO_4]$ (100 mg, 0.192 mmol) and $Ph_2P(S)H$ (42 mg, 0.192 mmol) in acetone (20 cm^3) was stirred for 30 min. The resulting red solution was concentrated under reduced pressure to *ca.* 2 cm^3; addition of diethyl ether led to the precipitation of a dark orange solid which was filtered off, washed with diethyl ether, and air-dried.

Complexes (**11a**) *and* (**11b**). To a mixture of $[(C_5Me_5)RhCl(acac)]$ (100 mg, 0.268 mmol) and $Ph_2P(S)H$ (58.6 mg, 0.268 mmol) in acetone or methanol (20 cm^3) was added $NaBPh_4$ (45.9 mg, 0.134 mmol). The starting material dissolved and after stirring for 5 min a red solid precipitated spontaneously. The resulting suspension was stirred for 20 min, after which the complex was filtered off, washed with acetone or methanol, and air-dried.

Complex (**12**). To a mixture of $[\{(C_5Me_5)RhCl\}_2(\mu\text{-}Cl)_2]$ (300 mg, 0.485 mmol) and $Ph_2P(S)H$ (635.5 mg, 2.912 mmol) in deoxygenated methanol (20 cm^3), KOH in methanol (5.9 cm^3, 0.164 mol dm^{-3}, 0.967 mmol) was added under a nitrogen atmosphere. The red complex precipitated spontaneously and was isolated after partial evaporation to *ca.* 10 cm^3. It was filtered off, washed with diethyl ether, and vacuum-dried.

Complex (**13**) *from* (**12**). Upon standing in methanol solution, complex (**12**) undergoes complete conversion into (**13**) within 24 h, giving red crystals which were isolated by filtration and air-dried.

Crystal Structure Determination of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}Cl)_2(\mu\text{-}Ph_2PS)][BPh_4]$.—*Crystal data.* $C_{56}H_{60}BCl_2PRh_2S$, triclinic, space group $P\bar{1}$, M = 1 083.65, a = 17.955 5(9), b = 15.581 5(9), c = 9.923 3(3) Å, α = 91.730(4), β = 96.962(4), γ = 95.087(4)° (by least-squares fit of the angular positions of 65 reflections with $2\theta < 90°$, Cu-K_α radiation), U = 2 742.6(2) $Å^3$, D_c = 1.312 g cm^{-3}, μ = 67.74 cm^{-1} [empirical absorption correction applied [24]]. A crystal of 0.37 × 0.17 × 0.07 mm was used to collect 7 581 independent reflections on a Philips PW 1100 diffractometer, with graphite-monochromated Cu-K_α radiation. Data were measured with ω—2θ scan amplitide of 1.5° and a detector aperture of 1.0 × 1.0°. The standard reflections monitored gave no significant variation during the collection time. 6 660 Reflections were considered as observed [$I > 3\sigma(I)$].

Solution and refinement. The structure was solved by Patterson analysis [25] and direct methods.[26] It was refined anisotropically by least-squares minimization of $\Sigma w\Delta^2$ with $w = 1$ initially. A weighting scheme was then applied to give no trends in $\langle w\Delta^2 F\rangle$ *versus* $\langle F_o\rangle$ or $\langle \sin\theta/\lambda\rangle$. The final R and R' [$R = (\Sigma w\Delta^2/\Sigma wF^2)^{\frac{1}{2}}$, $\Delta = |F_o| - |F_c|$] were 0.035 and 0.038 respectively. The H atoms were located from a difference synthesis and

included isotropically in the refinement. The final ΔF map showed no electron-density peaks greater than 0.56 e $Å^{-3}$.

Final atomic co-ordinates for the non-hydrogen atoms are given in Table 4. The scattering factors were taken from ref. 27. All calculations were done on a VAX 11/750 computer using mostly the *X*-RAY 76 system.[25]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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