

# Diphenylphosphino(phenylthio)methane as a monodentate or bidentate chelate ligand in rhodium, iridium and ruthenium complexes, crystal structure of $[(\eta^5-C_5Me_5)$ IrCl $(\eta^2-Ph_2PCH_2SPh-P,S)]BF_4 \cdot Me_2CO$

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Abstract—Reactions of complexes [{ $(\eta^5-C_5Me_5)MCl_2$ }] (M = Rh, Ir) and [{ $(\eta^6-MeC_6H_4Pr^i)RuCl_2$ }] with the ligand Ph<sub>2</sub>PCH<sub>2</sub>SPh in acetone solution led to neutral complexes with the general formula [(ring)MCl<sub>2</sub>( $\eta^1$ -Ph<sub>2</sub>PCH<sub>2</sub>SPh—P)] (1–3). These compounds react with thallium tetrafluoroborate in acetone solution to yield new cationic complexes in which the ligand is acting in its chelate P,S-donor fashion, [(ring)MCl( $\eta^2$ -Ph<sub>2</sub>PCH<sub>2</sub>SPh—P,S)]BF<sub>4</sub> (4–6). When the removal of the chloride ligand in complexes 1–3 was carried out in the presence of a stoichiometric amount of Ph<sub>2</sub>PCH<sub>2</sub>SPh, cationic compounds containing two P-donor monodentate ligands of the type [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)MCl ( $\eta^1$ -Ph<sub>2</sub>PCH<sub>2</sub>SPh—P)<sub>2</sub>]BF<sub>4</sub> (7 and 8) were obtained. The structure of the iridium derivative [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)IrCl( $\eta^2$ -Ph<sub>2</sub>PCH<sub>2</sub>SPh—P,S)]BF<sub>4</sub>·Me<sub>2</sub>CO has been determined by single-crystal X-ray diffraction methods. The complex cation contains a C<sub>5</sub>Me<sub>5</sub> group occupying three coordination positions of a distorted octahedral iridium centre, a bidentate chelate P,S-bonded ligand and a chloride atom completing the coordination sphere. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: diphenylphosphino(phenylthio)methane; rhodium; indium; ruthenium.

There is currently much interest in the synthesis of mono- and bimetallic platinum-group metal complexes containing, short-bite, unsymmetrical ligands such as (diphenylarsino)(diphenylphosphino)methane,[1] 2-(diphenylphosphino)pyridine,[2] diphenylphosphino(methylthio)methane,[3] diphenylphosphino(benzylthio)methane [4] and diphenylphosphino-(phenylthio)methane [5].

In particular, the P and S donor site ligands are described as monodentate P-donor ligands in Pd<sup>II</sup>, Pt<sup>II</sup>, Rh<sup>I</sup> and Ir<sup>I</sup> complexes, or as bidentate bridging P,S-donor ligands in bimetallic complexes with similar (Pd—Pd, Pt—Pt, Rh—Rh) or dissimilar (Pd—Rh) metal centres [3–5]. In these compounds the ligands acquire a head-to-tail arrangement and the metal centres are bonded by a metal-metal bond. However,

only few examples of complexes with these ligands acting in its chelate bidentate form are reported.

In this paper we describe the preparation of mononuclear neutral complexes of the general formula  $[(ring)MCl_2(\eta^1-Ph_2PCH_2SPh-P)]$  $[(ring)M = (\eta^{5} C_5Me_5$ )Rh (1), ( $\eta^5$ - $C_5Me_5$ )Ir (2), ( $\eta^6$ -*p*-MeC<sub>6</sub>H<sub>4</sub>Pr<sup>i</sup>)Ru (3)] and the related cationic complexes of the types  $[(ring)MCl(\eta^2-Ph_2PCH_2SPh-P,S)]BF_4$  [(ring)M = $(\eta^{5}-C_{5}Me_{5})Rh$  (4),  $(\eta^{5}-C_{5}Me_{5})Ir$  (5),  $(\eta^{6}-p-MeC_{6}H_{4})$ Pr<sup>i</sup>)Ru  $[(ring)MCl(\eta^1-Ph_2PCH_2)]$ (6)] and  $SPh-P_{2}BF_{4}$  [(ring)M = ( $\eta^{5}-C_{5}Me_{5}$ )Rh (7), ( $\eta^{5} C_5Me_5$  Ir (8)]. The structure of the complex [( $\eta^5$ - $C_5Me_5$ ]IrCl( $\eta^2$ -Ph<sub>2</sub>PCH<sub>2</sub>SPh-P,S)]BF<sub>4</sub>, determined by single-crystal X-ray diffraction, is also reported.

## **EXPERIMENTAL**

Elemental analyses (C, H and S) were made with a Perkin–Elmer 240C microanalyser. IR spectra were

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recorded on a Bruker IFS-25 spectrophotometer using KBr pellets. Conductivities were measured in *ca*  $5 \times 10^{-4}$  M acetone solutions using a WTW LF-521 conductimeter. <sup>1</sup>H (200 MHz) and <sup>31</sup>P <sup>1</sup>H (81 MHz) NMR spectra were recorded on a Bruker AC-200P spectrometer and the chemical shifts are reported in ppm relative to Me<sub>4</sub>Si and 85% H<sub>3</sub>PO<sub>4</sub> (positive shifts downfield) in D<sub>2</sub>O as internal and external standards, respectively.

All reactions were carried out by Schlenk techniques under purified nitrogen. Reagent-grade solvents were dried, distilled and stored under a nitrogen atmosphere. The starting complexes  $[{(\eta^{5}-C_{5}Me_{5})MCl_{2}}_{2}]$  (M = Rh, Ir),[6]  $[{(\eta^{6}-MeC_{6}H_{4} Pr^{i})RuCl_{2}}_{2}]$  [7] and the ligand Ph<sub>2</sub>PCH<sub>2</sub>SPh [5b] were prepared by published procedures.

Preparation of  $[(\eta^5-C_5Me_5)MCl_2(\eta^1-Ph_2PCH_2 SPh-P)]$  [M = Rh (1), Ir (2)]

1: To a suspension of the binuclear complex [ $\{(\eta^5 C_5 Me_5)RhCl_2\}_2$ ] (124 mg, 0.2 mmol) in acetone (10 cm<sup>3</sup>) the ligand Ph<sub>2</sub>PCH<sub>2</sub>SPh (123 mg, 0.4 mmol) was added with an immediate formation of a red solid. After stirring the mixture for 1 h, the solid complex was filtered off, washed with diethylether and airdried. The complex was recrystallized from chloroform-diethylether. Yield: 167 mg (68%). Found: C, 56.8; H, 5.7; S, 5.3. Calc. for C<sub>29</sub>H<sub>32</sub>Cl<sub>2</sub>PRhS: C, 56.4; H, 5.2; S, 5.2%.

**2**: To a solution of the binuclear complex  $[\{(\eta^5 C_5 Me_5)IrCl_2\}_2]$  (159 mg, 0.2 mmol) in dichloromethane (15 cm<sup>3</sup>) was added the ligand Ph<sub>2</sub>PCH<sub>2</sub> SPh (123 mg, 0.4 mmol). The colour of the solution changed from orange to yellow. The solution was stirred at room temperature for 1 h and then evaporated to a small volume (3–5 cm<sup>3</sup>). The addition of *n*-hexane caused the precipitation of a yellow solid, which was filtered off, washed with *n*-hexane and crystallized from dichloromethane–*n*-hexane. Yield: 240 mg (85%). Found: C, 49.1; H, 4.2; S, 4.7. Calc. for C<sub>29</sub>H<sub>32</sub>Cl<sub>2</sub>PIrS: C, 49.4; H, 4.6; S, 4.7%.

Preparation of  $[(\eta^6-MeC_6H_4Pr^i)RuCl_2(\eta^1-Ph_2PCH_2SPh-P)]$  (3)

To a solution of complex  $[{(n^6-MeC_6H_4 Pr^i)RuCl_2}_2]$  (122 mg, 0.2 mmol) in dichloromethane (15 cm<sup>3</sup>) a stoichiometric amount of the ligand Ph<sub>2</sub>PCH<sub>2</sub>SPh (123 mg, 0.4 mmol) was added and the mixture was stirred for 1 h. The solution obtained was concentrated and chromatographed on Kieselgel (HF<sub>254</sub> type 60) using CHCl<sub>3</sub>: *n*-hexane (2 : 1) as eluent. The solution was evaporated to dryness, the residue extracted with CHCl<sub>3</sub>, and the complex isolated as red crystals by addition of *n*-hexane. Yield: 215 mg (87%). Found: C, 56.8; H. 4.9; S. 5.1. Calc. for C<sub>29</sub>H<sub>31</sub>Cl<sub>2</sub>P-RuS: C, 56.7; H, 5.1; S, 5.2%.

Preparation of  $[(\eta^{5}-C_{5}Me_{5})MCl(\eta^{2}-Ph_{2}PCH_{2}SPh-P,S)]BF_{4}[M = Rh (4), Ir (5)]$ 

To a solution of complex 1 or 2 (0.15 mmol) in acetone (10 cm<sup>3</sup>) was added a stoichiometric amount of TlBF<sub>4</sub> (44 mg, 0.15 mmol). The resulting mixture was stirred for 8 h. During this time TlCl was precipitated and the colour of the solution changed from orange (1) or yellow (2) to pale yellow. The solution was filtered off through Kieselguhr, concentrated to a small volume and the complexes precipitated by addition of diethylether or n-hexane. (4) Orange crystals from chloroform-diethylether. Yield: 70 mg (69%). Found: C, 51.5; H, 4.3; S, 4.9. Calc. for  $C_{29}H_{32}BClF_4PRhS$ : C, 52.0; H, 4.8; S, 4.8%.  $\Lambda = 131$  $cm^2 mol^{-1} ohm^{-1}$ . 5: Yellow crystals from acetonediethylether-pentane. Yield: 109 mg (96%). Found: C, 46.9; H, 4.5; S, 4.0. Calc. for C<sub>29</sub>H<sub>32</sub>BClF<sub>4</sub>PIrS  $\cdot C_3 H_6 O: C, 47.1; H, 4.7; S, 3.9\%. \Lambda = 126 \text{ cm}^2 \text{ mol}^{-1}$ ohm<sup>-1</sup>.

Preparation of  $[(\eta^6-MeC_6H_4Pr^i)RuCl(\eta^2-Ph_2PCH_2SPh-P,S)]BF_4$  (6)

To a solution of complex **3** (92 mg, 0.15 mmol) in acetone (15 cm<sup>3</sup>) was added a stoichiometric amount of TlBF<sub>4</sub> (44 mg, 0.15 mmol). After stiring the mixture for 12 h, the TlCl formed was filtered off through Kieselghur and the solution evaporated to a small volume. Careful addition of *n*-hexane gave red–orange crystals. Yield: 70 mg (70%). Found: C, 52.2; H, 4.9; S, 4.7. Calc. for C<sub>29</sub>H<sub>31</sub>BClF<sub>4</sub>PRhS: C, 52.3; H, 4.7; S, 4.8%.  $\Lambda = 141$  cm<sup>2</sup> mol<sup>-1</sup> ohm<sup>-1</sup>.

Preparation of  $[(\eta^5-C_5Me_5)MCl(\eta^1-Ph_2PCH_2SPh-P)_2]BF_4 [M = Rh (7), Ir (8)]$ 

To a solution of 0.1 mmol of complex 1 (62 mg) or 2 (70 mg) in acetone solution (10 cm<sup>3</sup>) was added the ligand Ph<sub>2</sub>PCH<sub>2</sub>SPh (31 mg, 0.1 mmol) and the stoichiometric amount of AgBF<sub>4</sub> (195 mg, 0.1 mmol). Solid AgCl was formed and the colour of the solution changed from orange to yellow. After stirring for 24 h the mixture was filtered off, the solution was concentrated to a small volume and the complexes precipitated as yellow solids by careful addition of *n*hexane. The complexes were filtered, washed with *n*hexane and dried *in vacuo.* 7: Yield: 33 mg (36 %). Found: C, 58.3; H, 5.3; S, 6.4. Calc. for C<sub>48</sub>H<sub>49</sub>BClF<sub>4</sub>P<sub>2</sub>RhS<sub>2</sub>: C, 59.0; H, 5.1; S, 6.6%. 8: Yield: 48 mg (48 %). Found: C, 53.5; H, 4.8; S, 6.0. Calc. for C<sub>48</sub>H<sub>49</sub>BClF<sub>4</sub>P<sub>2</sub>IrS<sub>2</sub>: C, 54.1; H, 4.6; S, 6.0%.

#### Crystal structure of complex 5

A yellow, parallelepiped-shaped crystal, of approximate dimensions  $0.22 \times 0.22 \times 0.20$  mm, obtained from a slow diffusion of diethylether into an acetone

solution of the complex, was selected for structure determination by X-ray diffraction. Intensity data were collected on a Siemens R3m/v diffractometer in  $\theta/2\theta$  scan mode, using graphite-monochromated Mo $K_z$  radiation ( $\lambda = 0.71073$  Å). 4492 reflections collected gave 4272 independent reflections ( $R_{int} = 0.0199$ ), of which 2899 had  $I < 2\sigma(I)$ . Semi-empirical corrections for absorption, via psi-scans, were applied to the intensities.

A summary of the crystal data and relevant refinement parameters are presented in Table 1. The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares calculations, using all 4272 reflections. Non-H atoms were refined anisotropically. H atoms were placed at geometrically idealized positions with C—H = 0.96 Å and were allowed to ride over their parent C atoms with the isotropic displacement parameter  $U_{iso}$  equal to the equivalent isotropic  $U_{eq}$  of the attached C atom. Final R(F) [ $I < 2\sigma(I)$ ] was 0.034. All calculations were performed with the Siemens SHELXTL [8] and SHELXL-93 [9] programs. The absolute structure was determined using SHELXL-93 routine to refine the Flack parameter x which converged to 0.001(9).

Tables of positional and thermal parameters, full list of bond distances and angles, short contacts, leastsquares planes with dihedral angles, and listing of observed and calculated structure factors have been deposited with the Editor as supplementary material.

### **RESULTS AND DISCUSSION**

The binuclear complexes  $[\{(\eta^5 C_5 M e_5) M C l_2\}_2]$ (M = Rh, Ir) and  $[\{\eta^6 - M e C_6 H_4 P r^i) R u C l_2\}_2]$  react with the ligand diphenylphosphino (phenylthio)methane,  $Ph_2PCH_2SPh$ , in acetone or dichloromethane solution by cleavage of the chlorine bridges to yield neutral complexes with the ligand acting as a unidentate P-donor ligand, in accord with the general equation:

 $1/2[{(ring)MCl_2}_2] + Ph_2PCH_2SPh \longrightarrow$ 

$$[(ring) MCl_2(\eta^1 - Ph_2PCH_2SPh-P)]$$

where (ring)M =  $(\eta^{5}-C_{5}Me_{5})Rh(1)$ ,  $(\eta^{5}-C_{5}Me_{5})Ir(2)$ and  $(\eta^{6}-p-MeC_{6}H_{4}Pr^{i})Ru(3)$ .

The <sup>1</sup>H NMR spectra of complexes 1–3 exhibit a doublet resonance in the range  $\delta$  4.1–4.4 ppm assigned to methylene protons of the ligand together with the expected signals of coordinated rings. Their <sup>31</sup>P <sup>1</sup>H NMR spectra show a doublet resonance for complex 1 and a singlet resonance for complexes 2 and 3. In all cases the signals are substantially shifted to low field compared to those of the free ligand (coordination shifts in the range  $\Delta \delta P = 21-54$  ppm). Relevant NMR chemical shifts and coupling constants are listed in Table 2.

Complexes 1-3 slowly react in acetone solution with thallium tetrafluoroborate at room temperature to give non soluble thallium chloride and the corresponding cationic complexes with the ligands acting in their bidentate chelate fashion, according to the general equation:

$$1-3 + TlBF_4 \longrightarrow [(ring)MCl(\eta^2-Ph_2PCH_2)]$$

SPh-P,S]BF<sub>4</sub> + TlCl

where (ring)M =  $(\eta^{5}-C_{5}Me_{5})Rh$  (4),  $(\eta^{5}-C_{5}Me_{5})Ir$  (5) and  $(\eta^{6}-p-MeC_{6}H_{4}Pr^{i})Ru$  (6).

Empirical formula	C <sub>32</sub> H <sub>38</sub> BClF <sub>4</sub> IrOPS
Formula weight	816.11
Crystal system	Orthorhombic
Space group	Pna2,
Unit cell dimensions	$a = 16.172(4)$ Å, $\alpha = 90.0^{\circ}$
	$b = 11.782(3)$ Å, $\beta = 90.0^{\circ}$
	$c = 17.754(4) \text{ Å}, \gamma = 90.0^{\circ}$
Volume (Å <sup>3</sup> )	3382.8(14)
Ζ	4
Density (calculated) (Mg $m^{-3}$ )	1.602
Absorption coefficient (mm <sup>-1</sup> )	4.181
F (000)	1616
heta range for data collection (°)	2.07-28.06
Index ranges	$0 \le h \le 21, 0 \le k \le 15, -23 \le l \le 0$
Absorption correction	Semi-empirical, via psi-scans
Maximum and minimum transmission	0.931 and 0.762
Data/restraints/parameters	4272/0/378
Weighting scheme	$1/[\sigma^2(F_o^2) + (0.0356 P)^2]$ , where $P = [Max(F_o^2, 0) + 2F_c^2]/3$
Goodness-of-fit on $F^2$	0.872
Final R indices $[I > 2\sigma(I)]$	$R(F) = 0.0339, wR(F^2) = 0.0641$
R indices (all data)	$R(F) = 0.0648, wR(F^2) = 0.0705$
Largest difference peak and hole (e $Å^{-3}$ )	1.111  and  -0.766

Table 1. Crystallographic data for complex 5

	'H		<sup>31</sup> P { <sup>1</sup> H}	
	Ring	$CH_2$	$\delta \mathbf{P}$	$\Delta \delta \mathbf{P}^{b}$
1	1.37 (d, C <sub>5</sub> Me <sub>5</sub> )	4.42 (d)	34.29 (d)	53.69
	${}^{4}J(\mathrm{PH}) = 3.52$	${}^{2}J(\mathrm{PH}) = 3.50$	$^{1}J(PRh) = 141.3$	
2	$1.37 (d, C_5 Me_5)$	4.45 (d)	1.68 (s)	21.08
	${}^{4}J(\mathrm{PH}) = 2.27$	${}^{2}J(\mathrm{PH}) = 4.54$		
3	0.80 (d, Me, Pr <sup>i</sup> )	4.17 (d)	29.52 (s)	48.92
	${}^{3}J(\mathrm{HH}) = 6.9$	${}^{2}J(\mathbf{PH}) = 3.50$		
	1.89 (s, Me)			
	2.51 (m, CH, Pr <sup>i</sup> )			
4	$1.66 (d, C_5 Me_5)$	$4.78 (m, H_a)$	-2.45 (d)	16.95
	${}^{4}J(\mathrm{PH}) = 4.40$	5.67 (m, H <sub>b</sub> )	${}^{1}J(\text{PRh}) = 120.5$	
5	$1.72 (d, C_5 Me_5)$	5.07 (dd, $H_a)^c$	-34.14 (s)	-14.74
	$^{4}J(\mathrm{PH}) = 2.93$	${}^{2}J(\mathrm{PH}_{\mathrm{a}}) = 10.51$		
		${}^{2}J(\text{HH}) = 12.20$		
6	1.03 (d, Me, Pr <sup>i</sup> )	$4.89 (dd, H_a)$	-1,72 (s)	17.68
	1.14 (d, Me, Pr <sup>i</sup> )	5.79 (dd, $H_{b}$ ) <sup>d</sup>		
	${}^{3}J(\text{HH}) = 6.9$	${}^{2}J(\mathbf{PH}_{a}) = 10.39$		
	1.85 (s, Me)	${}^{2}J(\mathrm{PH}_{\mathrm{b}}) = 8.16$		
	2.41 (m, CH, Pr <sup>i</sup> )	${}^{2}J(HH) = 11.83$		
7	$1.26 (t, C_5 Me_5)$	3.24 (m, 2H) 3.80 (m, 2H)	26.64 (d)	46.04
	${}^{4}J(\mathrm{PH}) = 3.60$		${}^{1}J(\text{PRh}) = 133.9$	
8	1.27 (t, C <sub>5</sub> Me <sub>5</sub> )	3.30 (m, 2H)	-10.85 (s)	8.55
	$^{4}J(\text{PH}) = 2.30$	3.83 (m, 2H)	. /	
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Table 2. NMR chemical shifts ( $\delta$  ppm) and coupling constants (Hz) of isolated complexes"

"Measured in CDCl<sub>3</sub> at room temperature. Chemical shifts relative to  $Me_4Si$  and  $H_3PO_4$  (85%) in  $D_2O$  as standards. s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; br, broad. All complexes show multiplets in the region 7.0–8.0 ppm corresponding to phenyl groups of the ligands.

 ${}^{b}\Delta\delta P = [\delta P(\text{monodentate complex}) \cdot \delta P(\text{free ligand})] \text{ (free ligand: } \delta P = -19.40 \text{ ppm}).$ 

<sup>c</sup>The resonance of the H<sub>b</sub> proton is masked by the signals of phenyl rings.

<sup>d</sup>This signal is superposed with those of the ring protons of the *p*-cymene ligand. This assignment was made with the aid of double irradiation techniques.

These cationic complexes were isolated as stable microcrystalline solids and behave as 1:1 electrolytes in acetone solution. Their 'H NMR spectra exhibit the expected resonances of the coordinated ring and two resonances which correspond to the non-equivalent protons  $H_a$  and  $H_b$ . The proton endo to the chlorine atom is labelled H<sub>a</sub> and is assigned to the highest field resonance on the basis of results obtained bis(difor related complexes containing phenylphosphine)methane(dppm) or their chalcogenides derivatives as chelate ligands [10]. Complex 5 shows only a doublet of doublets at  $\delta$  5.07 ppm for the  $H_a$  proton. The  $H_b$  proton appears in the range  $\delta$ 7.0–8.0 ppm and is masked by the phenyl resonances of the ligand. This assignment is based on the NMR results obtained for the similar complex  $[(\eta^{5} C_5Me_5$ ]IrCl( $\eta^2$ -MeSCH<sub>2</sub>SMe—S,S)]BF<sub>4</sub>, which shows two doublet resonances for the methylene protons at  $\delta$  5.56 (H<sub>a</sub>) and 7.28 (H<sub>b</sub>) ppm [11]. The <sup>1</sup>H NMR spectrum of complex 6 shows two doublets of doublets resonances assigned to H<sub>a</sub> and H<sub>b</sub> with their corresponding different  ${}^{2}J(PH)$  couplings.

The <sup>31</sup>P {<sup>1</sup>H} NMR of complexes **4–6** show a shift of the signals to high field respect to the starting neutral complexes **1–3**, respectively. The large shielding of P atom ( $\Delta \delta P = 31-37$  ppm) is the typical behaviour of a coordinated P atom, which is part of a four-membered chelate ring, where the conformational change produces an increase in their electron density [12]. The decrease in the value of the phosphorus-rhodium coupling constant in complex **4** [<sup>1</sup>J(RhP) = 120.5 Hz] with respect to complex **1** [<sup>1</sup>J(RhP) = 141.3 Hz] suggests that the formation of the chelate ring causes a decrease of the  $\sigma$  character of the metal–phosphorus bond.

The addition of an excess of the ligand Ph<sub>2</sub>PCH<sub>2</sub>SPh to an acetone solution of complexes **4** and **5** causes the cleavage of the labile metal-thioether bond to form new cationic complexes in which the ligands are acting in their monodentate P-donor form,  $[(\eta^5-C_5Me_5)MCl(\eta^1-Ph_2PCH_2SPh-P)_2]BF_4$ , where M = Rh (7) and Ir (8). These compounds have not been isolated as pure samples by this synthethic method and always contain traces of the cor-



responding starting derivatives. However, the direct reaction of complexes 1 and 2 with a stoichiometric amount of the ligand in the presence of  $TIBF_4$  led only to the formation of complexes 7 and 8, respectively. All these reactions are represented in Scheme 1.

At room temperature (25°C) the <sup>1</sup>H NMR spectra of complexes 7 and 8 exhibit the expected triplet resonance for the permethylated ring and two broad multiplet resonances assigned to different methylene protons. When the temperature is raised to 60°C, these broad signals split in a doublet of multiplets with a  ${}^{2}J(HH) \simeq 14.5$  Hz. With cooling at -60°C only very broad signals were observed. The  ${}^{31}P$  {<sup>1</sup>H} NMR spectra at room temperature show a doublet and singlet resonances for complexes 7 and 8, respectively. The doublet signal shown by complex 7, centred at  $\delta$  26.64 ppm ['J(RhP) = 133.9 Hz], is shifted to high field respect to that of the starting complex 1 [ $\delta$  34.29 ppm; 'J(RhP) = 141.3 Hz], indicating the existence of  $\pi$ -backbonding from the metal centre to the phosphorus atom. This effect causes a decrease of the  $\sigma$  character of the Rh—P bond and, consequently, a decrease of the phophorus-rhodium coupling.

In order to obtain an unambiguous characterization of complex 5, an X-ray diffraction study was undertaken. Table 3 lists the relevant bonds distances and angles. Figure 1 shows a perspective ORTEP view of the cation, showing the metal centre with a pseudooctahedral geometry, commonly referred as "threelegged piano stool" configuration, with the centroid of the pentamethylcyclopentadienyl ligand occupying the centre of three octahedral sites, the diphenylphosphino(phenylthio)methane ligand bonded to the iridium atom through the phosphorus and sulfur atoms and a chloride atom completing the coordination sphere.

The methyl substituents are bent away from the iridium atom and the Ir—C(ring) distances span the range 2.161(7)–2.238(8) Å and compares well with those found in other pentamethylcyclopentadienyl iridium complexes [8b,13].

The Ir-S distance, 2.402(3) Å, is larger than those found in the thioether-iridium(III) complex [IrCl(1,4,8,11-tetrathiocyclotetradecane)]BPh<sub>4</sub> [average: 2.293(4) Å],[14] and is similar to the distances found in the thiolate complex  $[Ir(S_2CNEt_2)_3]$  [average: 2.370(2) Å][15] and the phosphine sulfide complex  $[(\eta^{5}-C_{5}Me_{5})Ir \{PO(OMe)_{2}\} \{\eta^{2}-(SPPh_{2})_{2}CH_{2}\}]BF_{4}$ [average: 2.398(2) Å].[8b] The Ir-P distance, 2.303(3) Å, compares well with those found in the phosphine-iridium(III) complexes  $[IrH(\eta^{1},\eta^{3} C_8H_{12}$  (dppm)] [lr—P: average 2.288(2) Å][16] and [IrCl<sub>2</sub>(CO)<sub>2</sub>( $\mu$ -CO)( $\mu$ -dppm)] [Ir - P:average 2.330(3) Å] [17]. The Ir-Cl separation, 2.381(2) Å, is similar to those found in related complexes containing the " $(C_5Me_5)$ Ir" moiety, as in the mono-

Ir—C(1)	2.229(9)	Ir—P	2.303(3)
Ir-C(2)	2.169(10)	Ir—S	2.402(3)
Ir - C(3)	2.174(9)	IrCl	2.381(2)
Ir—C(4)	2.161(7)	Р—С	1.854(9)
Ir - C(5)	2.238(8)	S—C	1.836(10)
P-C(11)	1.819(9)	PC(21)	1.823(14)
S-C(31)	1.781(10)		
P—Ir—Cl	86.99(9)	S—C—P	96.4(5)
P—Ir—S	71.51(9)	Ir—S—C	91.6(3)
Cl-—Ir-—S	89.59(9)	Ir—P—C	94.3(3)
IrSC(31)	118.0(4)	Ir - P - C(11)	122.1(3)
lr—P—C(21)	118.4(4)	C(11)—P—C(21)	105.5(5)

Table 3. Selected bond lengths (Å) and bond angles (°), with e.s.d.s in parentheses



Fig. 1. ORTEP view of the cation in complex 5, with 40% probability ellipsoids and atom numbering. H atoms are drawn as circles of arbitrary radius.

nuclear complexes  $[(\eta^5-C_5Me_5)IrCl(L-prolinate)]$ [Ir--Cl: 2.417(3) Å] and  $[(\eta^5-C_5Me_5)IrCl(L-his$ tidine)]Cl [Ir--Cl: 2.402(5) Å] [18].

The P—C [1.854(9) Å] and S—C [1.836(10) Å] distances in the coordinated chelate ligand are similar to those found in the A-frame complexes containing the related bidentate bridging ligand Ph<sub>2</sub>PCH<sub>2</sub> SCH<sub>2</sub>Ph, [Pd<sub>2</sub>Cl<sub>2</sub>( $\mu$ -Ph<sub>2</sub>PCH<sub>2</sub>SCH<sub>2</sub>Ph)] [P—C: 1.87(2) and P—S: 1.77(3) Å][4b] and [Rh<sub>2</sub>Cl<sub>4</sub>(CO)<sub>2</sub>( $\mu$ -Ph<sub>2</sub>PCH<sub>2</sub>SCH<sub>2</sub>Ph)] [P—C: 1.840(5) and P—S: 1.813(3) Å] [4a]. However, the angle P—C—S 96.4(5)°, is smaller than the corresponding angle observed in the ligand of the above mentioned A-frame complexes: P—C—S: 104.2(8) and 108.3(8)°, respectively.

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