

Tris(diphenylthiophosphinoyl) methanide as tripod ligand in rhodium(III), iridium(III) and ruthenium(II) complexes. Crystal structures of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}\{\eta^3\text{-(SPPPh}_2)_3\text{C-S,S',S''}\}]\text{BF}_4$  and  $[(\eta^6\text{-MeC}_6\text{H}_4\text{Pr}^i)\text{Ru}\{\eta^3\text{-(SPPPh}_2)_3\text{C-S,S',S''}\}]\text{BPh}_4$

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Abstract

Reaction of the complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2]_2$ , in  $\text{CH}_2\text{Cl}_2$  solution, with  $\text{AgBF}_4$  (1:2 molar ratio) and  $(\text{SPPPh}_2)_3\text{CH}$  leads to the cationic compound  $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}\{\eta^2\text{-(SPPPh}_2)_2\text{CH(SPPPh}_2\text{-S,S'})}\}\text{BF}_4$  (**1**) which is deprotonated by thallium(I) pyrazolate affording  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}\{\eta^3\text{-(SPPPh}_2)_3\text{C-S,S',S''}\}]\text{BF}_4$  (**2a**). The iridium dimer  $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}_2]_2$  reacts with silver salts and  $(\text{SPPPh}_2)_3\text{CH}$ , in  $\text{CH}_2\text{Cl}_2$  or  $\text{Me}_2\text{CO}$ , under analogous conditions, affording mixtures of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}\{\eta^2\text{-(SPPPh}_2)_2\text{CH(SPPPh}_2\text{-S,S'})}\}]^+$  and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}\{\eta^3\text{-(SPPPh}_2)_3\text{C-S,S',S''}\}]\text{A}$  [ $\text{A} = \text{BF}_4^-$  (**3a**),  $\text{PF}_6^-$  (**3b**)]. Addition of  $\text{Et}_3\text{N}$  to the mixture gives pure complexes **3**. The ruthenium complexes  $[(\eta^6\text{-arene})\text{RuCl}_2]_2$  (arene =  $\text{C}_6\text{Me}_6$ ,  $p\text{-MeC}_6\text{H}_4\text{Pr}^i$ ) react with  $(\text{SPPPh}_2)_3\text{CH}$ , in the presence of  $\text{AgA}$  ( $\text{A} = \text{PF}_6^-$  or  $\text{BF}_4^-$ ) or  $\text{Na BPh}_4$ , in  $\text{CH}_2\text{Cl}_2$  or  $\text{Me}_2\text{CO}$ , yielding only the deprotonated complexes  $[(\eta^6\text{-arene})\text{Ru}\{\eta^3\text{-(SPPPh}_2)_3\text{C-S,S',S''}\}]\text{A}$  [arene =  $\text{C}_6\text{Me}_6$ ,  $\text{A} = \text{BF}_4^-$ ; arene =  $p\text{-MeC}_6\text{H}_4\text{Pr}^i$ ,  $\text{A} = \text{BPh}_4$  (**4a**),  $\text{PF}_6^-$  (**4b**)]. The crystal structures of **3a** and **4a** were established by X-ray crystallography. Compound **3a** crystallizes in the orthorhombic space group  $Pna2_1$ , with lattice parameters  $a = 41.477(6)$ ,  $b = 10.6778(11)$ ,  $c = 20.162(3)$  Å and  $Z = 8$ . Complex **4a** crystallizes in a monoclinic lattice, space group  $P2_1/n$ , with  $a = 20.810(4)$ ,  $b = 12.555(3)$ ,  $c = 23.008(4)$  Å,  $\beta = 95.82(2)^\circ$  and  $Z = 4$ . Both cationic complexes exhibit analogous *pseudo*-octahedral molecular structures with the anionic  $(\text{SPPPh}_2)_3\text{C}^-$  ligand bonded via the three sulphur atoms in a tripodal, tridentate fashion. Each metal centre completes its coordination environment with a  $\eta^5\text{-C}_5\text{Me}_5$  (**3a**) or a  $\eta^6\text{-MeC}_6\text{H}_4\text{Pr}^i$  group (**4a**). A quite interesting result concerns the non-planarity of the methanide carbon which display P–C–P angles in the range  $112.6\text{--}114.4(5)^\circ$  in **3a** and  $111.9\text{--}113.6(4)^\circ$  in **4a**. The redox chemistry of the complexes was investigated by cyclic voltammetry. The Rh(III) complexes are quasi-reversibly reduced to Rh(I) and the Ir(III) complex is irreversibly reduced to Ir(I) in acetonitrile solutions. The Ru(II) complex undergoes a quasi-reversible reduction to Ru(I) and a reversible oxidation to Ru(III). © 1997 Elsevier Science S.A.

Keywords: Rhodium; Iridium; Ruthenium; Pentamethylcyclopentadienyl complexes; Chalcogenide ligands

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## 1. Introduction

There is considerable interest in the coordination properties of chalcogenide ligands, derived from tertiary di- and triphosphines, of the types  $(\text{EPh}_2)_2\text{CRH}$  ( $\text{E} = \text{S}, \text{Se}$ ) and  $(\text{EPh}_2)_3\text{CH}$  ( $\text{E} = \text{O}, \text{S}, \text{Se}$ ) [1–24]. The methylene or methine protons of the free or coordinated ligands can be abstracted by bases affording anionic species of formulae  $[(\text{EPh}_2)_2\text{CR}]^-$  or  $[(\text{EPh}_2)_3\text{C}]^-$  which display a variety of coordination modes. Thus, for example,  $[(\text{EPh}_2)_2\text{CH}]^-$  species act as bidentate  $\text{E}, \text{E}'$ -donor ligands in  $\text{Cu}(\text{II}), \text{Fe}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{I}), \text{Rh}(\text{I}), \text{Ir}(\text{I})$  and  $\text{Pd}(\text{II})$  chemistry [5–8] or, also as bidentate, but  $\text{C}, \text{S}$ -donor ligands, in  $\text{Pt}(\text{II})$  compounds [9–11]. Additionally, they can act as tridentate  $\text{C}, \text{S}, \text{S}'$ -bridging six-electron ligands toward  $\text{Au}(\text{I})$  [12]. Similarly, the anionic derivative  $[(\text{SPh}_2)_3\text{C}]^-$  acts as a  $\eta^2\text{-S}, \text{S}'$ -donor ligand toward  $d^8$  metal centres [ $\text{Rh}(\text{I}), \text{Ir}(\text{I})$  and  $\text{Pt}(\text{II})$ ] [18–21] while it behaves as a tripodal  $\text{S}, \text{S}', \text{S}''$ -donor ligand to  $d^{10}$  soft metals such as  $\text{Ag}(\text{I}), \text{Hg}(\text{II})$  or  $\text{Cd}(\text{II})$  [22–24].

We recently reported that the anionic ligands  $[(\text{EPh}_2)_2\text{CH}]^-$  can act as tridentate  $\text{C}, \text{E}, \text{E}'$ -donor ligands in  $(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{III}), (\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{III}),$  and  $(\eta^6\text{-arene})\text{Ru}(\text{II})$  complexes [13–16] and that the related methyl substituted ligand  $[(\text{EPh}_2)_2\text{CMe}]^-$  displays a similar coordination behaviour in  $(\eta^6\text{-arene})\text{Ru}(\text{II})$  compounds [17]. Following our studies on the coordination chemistry and ligand behaviour of these types of ligands, in this paper, we describe the synthesis and characterization of new  $(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{III}), (\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{III}),$  and  $(\eta^6\text{-arene})\text{Ru}(\text{II})$  complexes with  $(\text{SPh}_2)_3\text{CH}$  and its methanide anion as ligands. The molecular structures of the complexes  $[(\eta\text{-ring})\text{M}(\eta^3\text{-}(\text{SPh}_2)_3\text{C-S}, \text{S}', \text{S}'')] \text{A}$  [ $(\eta\text{-ring})\text{M} = (\eta^5\text{-C}_5\text{Me}_5)\text{Ir}, \text{A} = \text{BF}_4$  (**3a**);  $(\eta\text{-ring})\text{M} = (\eta^6\text{-MeC}_6\text{H}_4\text{Pr}^i)\text{Ru}, \text{A} = \text{BPh}_4$  (**4a**)], determined by single crystal X-ray diffraction methods, are also reported. Moreover the electrochemical behaviour of the new complexes is studied by cyclic voltammetry.

## 2. Experimental details

### 2.1. General

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  $[(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}_2]$  ( $\text{M} = \text{Rh}, \text{Ir}$ ) [25],  $[(\eta^6\text{-arene})\text{RuCl}_2]$  (arene =  $\text{C}_6\text{Me}_6,$   $p\text{-MeC}_6\text{H}_4\text{Pr}^i$ ) [26] and the ligand  $(\text{SPh}_2)_3\text{CH}$  [27] were prepared by published procedures.

Elemental analyses were made with a Perkin–Elmer 240C microanalyser. IR spectra were 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.  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker AC-200P and a Varian 250 spectrometers. Chemical shifts are reported in ppm relative to  $\text{Me}_4\text{Si}$  and 85%  $\text{H}_3\text{PO}_4$  (positive shifts downfield), respectively. Mass spectra were measured on a VG Autospec double-focusing mass spectrometer operating in the  $\text{FAB}^+$  mode. Ions were produced with the standard  $\text{Cs}^+$  gun at ca. 30 Kv, and 3-nitrobenzyl alcohol (NBA) was used as matrix.

Cyclic voltammetric (CV) measurements were carried out with a Potentiostat Bank (Model Wenking ST-72) coupled to a Voltage Scan Generator (Model USG-72) and a Graphtec Recorder (Model WX-1100). Bulk electrolyses were performed with a Voltage Integrator Bank (Model Wenking EVI-80). The working electrode used in the CV was a platinum inlay electrode (Beckman). The auxiliary electrode was a platinum-coil electrode, which was isolated from the bulk solution by a glass tube with a porosity glass frit at the end; it contained alumina and 0.2 molar solution of supporting electrolyte. The reference was a  $\text{Ag}/\text{AgCl}$  (aqueous tetramethylammonium chloride) cracked glass bead electrode, which was adjusted to 0.00 vs. the saturated calomel electrode (SCE) [28]. The reference electrode was located inside a Luggin capillary in the cell compartment. For controlled-potential electrolysis, a platinum-mesh working electrode was used for the ruthenium compound and a pyrolytic graphite electrode for the rhodium and iridium derivatives.

All the experiments were performed under an argon atmosphere, at room temperature ( $20^\circ\text{C}$ ), in acetonitrile solution. Solutions were 1 mM in complex and 200 mM in tetraethylammonium perchlorate (TEAP) as the supporting electrolyte.

### 2.2. Preparation of $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}\{\eta^2\text{-}(\text{SPh}_2)_2\text{CH}(\text{SPh}_2)\text{-S}, \text{S}'\}]\text{BF}_4$ (**1**)

A mixture of the rhodium complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2]$  (100.1 mg, 0.162 mmol) and  $\text{AgBF}_4$  (62.0 mg, 0.324 mmol), in  $\text{CH}_2\text{Cl}_2$  (25  $\text{cm}^3$ ), was stirred for 1 h at room temperature, in the absence of light. The precipitated silver chloride was removed by filtration through Kieselghur and, to the resulting solution,  $(\text{SPh}_2)_3\text{CH}$  (215.4 mg, 0.324 mmol) was added. After 1 h, the solution was concentrated to a small volume and  $n$ -hexane was added to precipitate a red solid. The product was recrystallized from dichloromethane-hexane. Yield: 254.2 mg (76%). Anal. Found: C, 54.7; H, 4.1; S, 9.5.  $\text{C}_{47}\text{H}_{46}\text{BClF}_4\text{P}_3\text{RhS}_3$ . Calc.: C, 55.0; H, 4.5; S, 9.4%. NMR ( $\text{CDCl}_3, 20^\circ\text{C}$ ):  $^1\text{H}$ ,  $\delta$  1.59 (15 H, s,  $\text{C}_5\text{Me}_5$ );  $^{31}\text{P}\{^1\text{H}\}$ ,  $\delta$  44.4 ppm (s, br). IR(KBr):  $\nu(\text{PS}), 548; \nu(\text{BF}_4^-), 1050, 515 \text{ cm}^{-1}$ .  $\Lambda_{\text{M}} = 147 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ .

2.3. Preparation of  $[(\eta^5\text{-C}_5\text{Me}_5)_M\{\eta^3\text{-(SPPPh}_2)_3\text{C-S,S',S''}\}]A$  [ $M = \text{Rh}$ ,  $A = \text{BF}_4^-$  (**2a**),  $\text{PF}_6^-$  (**2b**);  $M = \text{Ir}$ ,  $A = \text{BF}_4^-$  (**3a**),  $\text{PF}_6^-$  (**3b**)]

The complexes can be prepared by the three alternative methods, described below.

(a) To a solution of complex **1** (50.2 mg, 0.05 mmol) in acetone (10 cm<sup>3</sup>) was added thallium pyrazolate (13.2 mg, 0.05 mmol). After stirring for 1 h, the thallium chloride formed was filtered off through Kieselghur and the solution was evaporated to a small volume. Complex **2a** was precipitated by adding *n*-hexane and recrystallized from dichloromethane-diethylether. Yield: 27.2 mg (55%). Anal. Found: C, 56.8; H, 4.4; S, 9.4. C<sub>47</sub>H<sub>45</sub>BF<sub>4</sub>P<sub>3</sub>RhS<sub>3</sub>. Calc.: C, 57.0; H, 4.6; S, 9.7%. NMR (CDCl<sub>3</sub>, 20°C): <sup>1</sup>H, δ 2.00 (15 H, s, C<sub>5</sub>Me<sub>5</sub>); <sup>31</sup>P{<sup>1</sup>H}, δ 44.4 ppm (s, <sup>2</sup>J(RhP) = 3.6 Hz). IR(KBr): ν(P=S), 550; ν(BF<sub>4</sub><sup>-</sup>), 1048, 510 cm<sup>-1</sup>. A<sub>M</sub> = 152 Ω<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>.

(b) A mixture of the iridium complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}_2]_2$  (100.4 mg, 0.126 mmol) and AgBF<sub>4</sub> (49.3 mg, 0.251 mmol), in Me<sub>2</sub>CO (25 cm<sup>3</sup>), was stirred for 1 h at room temperature, in the absence of light. The precipitated silver chloride was removed by filtration through Kieselghur. The resulting solution was stirred with (SPPPh<sub>2</sub>)<sub>3</sub>CH (167.0 mg, 0.251 mmol) and an excess of triethylamine (0.15 cm<sup>3</sup>). Complex **3a** was precipitated by adding diethylether and recrystallized from dichloromethane-hexane. Yield 108.3 mg (40%). Anal. Found: C, 51.8; H, 3.9; S, 8.6. C<sub>47</sub>H<sub>45</sub>BF<sub>4</sub>IrP<sub>3</sub>S<sub>3</sub>. Calc.: C, 52.2; H, 4.2; S, 8.9%. NMR (CDCl<sub>3</sub>, 20°C): <sup>1</sup>H, δ 2.04 (15 H, s, C<sub>5</sub>Me<sub>5</sub>); <sup>31</sup>P{<sup>1</sup>H}, δ 42.4 ppm (s). IR(KBr): ν(P=S), 550; ν(BF<sub>4</sub><sup>-</sup>), 1050, 512 cm<sup>-1</sup>. A<sub>M</sub> = 107 Ω<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>.

(c) A solution of the binuclear complexes  $[(\eta^5\text{-C}_5\text{Me}_5)_M\text{Cl}_2]_2$  (0.08 mmol), in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>), was treated with AgPF<sub>6</sub> (82.0 mg, 0.32 mmol), in Me<sub>2</sub>CO, (5 cm<sup>3</sup>) and stirred for 1 h at room temperature in the absence of light. (SPPPh<sub>2</sub>)<sub>3</sub>CH (215.4 mg, 0.324 mmol) was added to the filtered solution and stirred again for 1 h (in the preparation of the Ir(III) complex a slight excess of Et<sub>3</sub>N was added). The solution was evaporated to dryness and the residue chromatographed on Kieselgel using acetone as eluent. The solution obtained was concentrated to a small volume and the complexes precipitated by adding diethylether. The products were recrystallized from dichloromethane-hexane. **2b**: Yield 163.2 mg (96%). Anal. Found: C, 53.5; H, 4.4; S, 9.0. C<sub>47</sub>H<sub>45</sub>F<sub>6</sub>P<sub>4</sub>RhS<sub>3</sub>. Calc.: C, 53.9; H, 4.4; S, 9.2%. NMR (CDCl<sub>3</sub>, 20°C): <sup>1</sup>H, δ 2.01 (15 H, s, C<sub>5</sub>Me<sub>5</sub>); <sup>31</sup>P{<sup>1</sup>H}, δ 43.0 (d, <sup>2</sup>J(RhP) = 3.3 Hz) and -144.8 ppm [sp, PF<sub>6</sub><sup>-</sup>, <sup>1</sup>J(PF) = 713 Hz]. IR(KBr): ν(PF<sub>6</sub><sup>-</sup>), 840 and 559 (masking P=S band) cm<sup>-1</sup>. A<sub>M</sub> = 123 Ω<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>. **3b**: Yield 177.0 mg (86%). Anal. Found: C, 49.4; H, 4.1; S, 8.5. C<sub>47</sub>H<sub>45</sub>F<sub>6</sub>P<sub>4</sub>IrS<sub>3</sub>. Calc.: C, 49.7; H, 4.0; S, 8.5%. NMR (CDCl<sub>3</sub>, 20°C): <sup>1</sup>H, δ

2.04 (15 H, s, C<sub>5</sub>Me<sub>5</sub>); <sup>31</sup>P{<sup>1</sup>H}, δ 41.0 (s) and -145.0 ppm [sp, PF<sub>6</sub><sup>-</sup>, <sup>1</sup>J(PF) = 712 Hz]. IR(KBr): ν(PF<sub>6</sub><sup>-</sup>), 840 and 554 (masking P=S band) cm<sup>-1</sup>. A<sub>M</sub> = 121 Ω<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>.

2.4. Preparation of  $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^i)\text{Ru}\{\eta^3\text{-(SPPPh}_2)_3\text{C-S,S',S''j}\}]\text{BPh}_4$  (**4a**)

A suspension of  $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^i)\text{RuCl}_2]_2$  (100.1 mg, 0.16 mmol), NaBPh<sub>4</sub> (112.3 mg, 0.33 mmol) and (Ph<sub>2</sub>PS)<sub>3</sub>CH (217.2 mg; 0.33 mmol), in acetone (25 cm<sup>3</sup>), was stirred at room temperature for 12 h. The mixture was filtered off through Kieselghur and evaporated to dryness. The solid residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> and chromatographed on Kieselgel using a mixture dichloromethane-acetone (12:1) as eluent. The solution obtained was concentrated to a small volume and the complex precipitated by careful addition of diethylether. Complex **4a** was recrystallized from dichloromethane-diethylether. Yield 319.2 mg (80%). Anal. Found: C, 70.6; H, 5.5; S, 7.8. C<sub>71</sub>H<sub>64</sub>BP<sub>3</sub>RuS<sub>3</sub>. Calc.: C, 70.0; H, 5.30; S, 7.9%. NMR (CDCl<sub>3</sub>, 20°C): <sup>1</sup>H, δ 1.49 [6H, d, <sup>3</sup>J(HH) = 6.9 Hz, 2Me(Pr<sup>i</sup>)], 2.32 (3H, s, Me), 3.15 [1H, sp, CH(Pr<sup>i</sup>)], 5.36 and 5.49 [4H, AB system, J(H<sub>A</sub>H<sub>B</sub>) = 6.0 Hz]; <sup>31</sup>P{<sup>1</sup>H}, δ 43.65 ppm (s). IR(KBr): ν(P=S), 556 cm<sup>-1</sup>. A<sub>M</sub> = 134 Ω<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>.

The related hexafluorophosphate complex  $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^i)\text{Ru}\{\eta^3\text{-(SPPPh}_2)_3\text{C-S,S',S''}\}]\text{PF}_6$  (**4b**) was prepared using AgPF<sub>6</sub> (87.2 mg, 0.34 mol) instead of NaBPh<sub>4</sub>. Yield 315.2 mg (93%). Anal. Found: C, 53.6; H, 4.2; S, 9.0. C<sub>47</sub>H<sub>45</sub>F<sub>6</sub>P<sub>4</sub>RuS<sub>3</sub>. Calc.: C, 54.0; H, 4.25; S, 9.2%. NMR (CDCl<sub>3</sub>, 20°C): <sup>31</sup>P{<sup>1</sup>H}, δ 43.5 (s) and -144.65 ppm [sp, PF<sub>6</sub><sup>-</sup>, <sup>1</sup>J(PF) = 712 Hz]. IR(KBr): ν 840 and 550 (masking P=S band) cm<sup>-1</sup>. A<sub>M</sub> = 128 Ω<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>.

2.5. X-ray crystallography study of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}\{\eta^3\text{-(SPPPh}_2)_3\text{C-S,S',S''}\}]\text{BF}_4$  (**3a**) and  $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^i)\text{Ru}\{\eta^3\text{-(SPPPh}_2)_3\text{C-S,S',S''}\}]\text{BPh}_4$  (**4a**)

#### 2.5.1. Crystal data for **3a**

C<sub>47</sub>H<sub>45</sub>BF<sub>4</sub>IrP<sub>3</sub>S<sub>3</sub>;  $M = 1077.9$ ; orthorhombic; space group *Pna*2<sub>1</sub>;  $a = 41.477(6)$ ,  $b = 10.6778(11)$ ,  $c = 20.162(3)$  Å,  $V = 8929(2)$  Å<sup>3</sup>,  $Z = 8$ ;  $D_c = 1.604$  mg m<sup>-3</sup>;  $F(000) = 4304$ ;  $\lambda(\text{Mo-K}\alpha) = 0.71073$  Å;  $\mu = 3.289$  mm<sup>-1</sup>;  $T = 293$  K.

#### 2.5.2. Crystal data for **4a**

C<sub>71</sub>H<sub>64</sub>BP<sub>3</sub>RuS<sub>3</sub>;  $M = 1218.2$ ; monoclinic, space group *P2*<sub>1</sub>/*n*;  $a = 20.810(4)$ ,  $b = 12.555(3)$ ,  $c = 23.088(4)$  Å,  $\beta = 95.82(2)^\circ$ ;  $V = 6001(2)$  Å<sup>3</sup>,  $Z = 4$ ;  $D_c = 1.348$  mg m<sup>-3</sup>;  $F(000) = 2528$ ;  $\lambda(\text{Mo-K}\alpha) = 0.71073$  Å;  $\mu = 0.489$  mm<sup>-1</sup>;  $T = 293$  K.

### 2.5.3. Data collection and processing

Suitable crystals for the X-ray determinations were grown up by slow diffusion of diethylether into dichloromethane solutions of complexes **3a** and **4a**. A yellow-orange triangular plate of approximate dimensions  $0.70 \times 0.63 \times 0.19$  mm was used in the analysis of **3a**; a red-orange parallelepiped-shaped crystal,  $0.18 \times 0.10 \times 0.20$  mm, in the case of **4a**. Intensity data were collected on a Siemens-Stoe AED-2 (**3a**) and a Siemens R3m/V (**4a**) diffractometers with graphite monochromated Mo-K $\alpha$  radiation. Cell parameters were determined by least-squares refinement from the  $2\theta$  values of 36 accurately centred reflections for **3a** ( $25 \leq 2\theta \leq 35^\circ$ ), and 30 reflections for **4a** ( $8 \leq 2\theta \leq 25^\circ$ ). A conventional  $\theta/2\theta$  scan mode was applied for the measurement of data in **4a**, whereas the long length of one cell parameter in **3a** suggested a  $\omega$ -scan to be more appropriate. A total of 22 439 reflections ( $4 \leq 2\theta \leq 50^\circ$ ) (**3a**) and 6186 reflections ( $3 \leq 2\theta \leq 40^\circ$ ) (**4a**) were collected; from 15 532 independent reflections ( $R_{\text{int}} = 0.0564$ ) 13 658 having  $I > 2\sigma(I)$  were considered observed and used in the analysis of **3a**; for complex **4a** 5622 independent reflections ( $R_{\text{int}} = 0.025$ ) of which 3563 with  $I > 1.5\sigma(I)$  were used in the analysis. A set of three standard reflections were monitored along both data collections as a check of crystal and instruments stability. Data were corrected for Lorentz and polarization effects. A semiempirical correction for absorption, via  $\psi$ -scans was applied to both sets of intensities (max. and min. trans. fact. 0.254 and 0.142, and 0.834 and 0.795 for **3a** and **4a**, respectively) [29].

### 2.5.4. Structure solution and refinement

The structures were solved by direct and Fourier methods (with SIR92 (**3a**) [30] or SHELXTL-PLUS (**4a**) [31]) and refined by full-matrix least-squares (SHELXL-93 [32] for **3a**, and SHELXTL-PLUS for **4a**). Atoms were refined isotropically first, and in subsequent cycles with anisotropic thermal parameters for all the non-hydrogen atoms. Four **3a** hydrogen atoms were included in calculated positions and refined riding on their respective carbon atoms with two common thermal parameters (one for the hydrogens of the C $_5$ Me $_5$  group and a second for those of the tridentate S-donor ligand). In the case of **4a**, hydrogens were refined analogously, but the displacement parameters were fixed to the isotropic equivalent of their respective parent carbons. A static disorder was observed in **3a** for the two independent BF $_4^-$  anions. Each independent anion was modeled on the basis of two BF $_4^-$  groups with restricted interatomic distances and complementary occupancy factors (0.51–0.49(4), and 0.61–0.39(7)). Weighting schemes were used in the final steps of the refinement:  $w^{-1} = [\sigma^2(F_o)^2 + (0.0456P)^2 + 36.9017P]$  where  $P = \max((0, F_c^2) + 2(F_c^2))/3$  for **3a**, and  $w^{-1} = \sigma^2(F_o)^2 + 0.00004F_o^2$  in **4a**. Refinements converged to  $R(F^2)$

$= 0.045$  and  $wR = 0.1165$  (all reflections included) for **3a** [32], and  $R(F) = 0.040$  and  $wR = 0.028$  for **4a** [31]. In the structural study of **3a**, a refinement of the Flack parameter  $x$  was carried out to estimate absolute struc-

Table 1

Selected atomic coordinates<sup>a</sup> ( $\times 10^4$ ,  $\times 10^5$  for Ir atoms) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^4$ ;  $\text{\AA}^2 \times 10^4$  for Ir, S and P atoms) for the complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^3\text{-SPPPh}_2)_3\text{C-S,S',S''}]_2\text{BF}_4$  (**3a**)

|        | <i>x</i>  | <i>y</i>  | <i>z</i>  | <i>U</i> <sub>eq</sub> <sup>b</sup> |
|--------|-----------|-----------|-----------|-------------------------------------|
| Ir(1)  | 55 860(1) | 58 695(3) | 71 934(2) | 325(1)                              |
| S(1)   | 5254(1)   | 6431(2)   | 6239(1)   | 429(6)                              |
| S(2)   | 5144(1)   | 5366(2)   | 7920(2)   | 411(5)                              |
| S(3)   | 5676(1)   | 3734(2)   | 6855(1)   | 411(6)                              |
| P(1)   | 4994(1)   | 4900(2)   | 5966(1)   | 366(5)                              |
| P(2)   | 4778(1)   | 4689(2)   | 7360(1)   | 360(5)                              |
| P(3)   | 5238(1)   | 2860(2)   | 6815(1)   | 330(5)                              |
| C(1)   | 5956(2)   | 7169(9)   | 6883(5)   | 39(2)                               |
| C(2)   | 5754(2)   | 7764(9)   | 7343(5)   | 43(2)                               |
| C(3)   | 5769(2)   | 7127(9)   | 7960(6)   | 43(2)                               |
| C(4)   | 5987(2)   | 6082(9)   | 7873(6)   | 45(2)                               |
| C(5)   | 6105(2)   | 6143(8)   | 7196(6)   | 43(2)                               |
| C(6)   | 6027(3)   | 7623(11)  | 6202(6)   | 66(3)                               |
| C(7)   | 5557(3)   | 8967(9)   | 7223(9)   | 56(3)                               |
| C(8)   | 5613(3)   | 7480(12)  | 8597(6)   | 62(3)                               |
| C(9)   | 6087(3)   | 5188(12)  | 8407(7)   | 72(4)                               |
| C(10)  | 6355(3)   | 5296(11)  | 6911(7)   | 63(3)                               |
| C(11)  | 4920(2)   | 3891(7)   | 6639(5)   | 35(2)                               |
| C(12)  | 5203(3)   | 4112(9)   | 5296(5)   | 42(2)                               |
| C(18)  | 4609(3)   | 5371(9)   | 5621(5)   | 42(2)                               |
| C(24)  | 4501(2)   | 5971(9)   | 7163(7)   | 45(2)                               |
| C(30)  | 4534(2)   | 3645(9)   | 7859(6)   | 48(2)                               |
| C(36)  | 5169(2)   | 2001(9)   | 7589(5)   | 40(2)                               |
| C(42)  | 5261(2)   | 1657(8)   | 6185(4)   | 36(2)                               |
| Ir(51) | 19 304(1) | 45 726(3) | 79 291(2) | 362(1)                              |
| S(51)  | 1836(1)   | 2460(2)   | 8330(1)   | 392(5)                              |
| S(52)  | 2256(1)   | 5210(2)   | 8875(1)   | 417(6)                              |
| S(53)  | 2391(1)   | 4080(2)   | 7232(2)   | 432(5)                              |
| P(51)  | 2270(1)   | 1588(2)   | 8367(1)   | 309(5)                              |
| P(52)  | 2503(1)   | 3683(2)   | 9186(1)   | 314(5)                              |
| P(53)  | 2746(1)   | 3382(2)   | 7823(1)   | 345(5)                              |
| C(51)  | 1535(3)   | 4729(9)   | 7234(8)   | 59(3)                               |
| C(52)  | 1418(2)   | 4853(11)  | 7912(8)   | 59(3)                               |
| C(53)  | 1563(3)   | 5906(11)  | 8205(6)   | 55(3)                               |
| C(54)  | 1763(3)   | 6456(10)  | 7745(6)   | 55(3)                               |
| C(55)  | 1750(2)   | 5786(11)  | 7146(7)   | 56(3)                               |
| C(56)  | 1438(4)   | 3853(15)  | 6705(9)   | 100(6)                              |
| C(57)  | 1160(3)   | 4006(14)  | 8217(10)  | 110(7)                              |
| C(58)  | 1482(4)   | 6355(16)  | 8908(8)   | 95(5)                               |
| C(59)  | 1945(4)   | 7658(11)  | 7889(11)  | 87(4)                               |
| C(60)  | 1913(4)   | 6129(15)  | 6524(8)   | 90(5)                               |
| C(61)  | 2583(2)   | 2633(8)   | 8536(4)   | 30(2)                               |
| C(62)  | 2332(2)   | 749(9)    | 7597(5)   | 38(2)                               |
| C(68)  | 2254(2)   | 379(8)    | 8991(4)   | 32(2)                               |
| C(74)  | 2283(2)   | 2898(9)   | 9862(4)   | 37(2)                               |
| C(80)  | 2884(2)   | 4173(9)   | 9541(5)   | 40(2)                               |
| C(86)  | 3030(2)   | 4639(8)   | 8014(5)   | 37(2)                               |
| C(92)  | 2990(2)   | 2260(9)   | 7376(5)   | 39(2)                               |

<sup>a</sup>The atomic coordinates of the phenyl groups—excepting those of the *ipso* carbons—and those of the disordered anions have been omitted.

<sup>b</sup> $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 2

Selected atomic coordinates<sup>a</sup> ( $\times 10^4$ ,  $\times 10^5$  for Ru atom) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ;  $\text{\AA}^2 \times 10^4$  for Ru, S and P atoms) for the complex  $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^i)\text{Ru}(\eta^3\text{-}(\text{SPPH}_2)_3\text{C-S,S',S''})]\text{BPh}_4$  (**4a**)

|       | x         | y        | z       | $U_{\text{eq}}^b$ |
|-------|-----------|----------|---------|-------------------|
| Ru    | 30 160(3) | 3716(5)  | 8029(3) | 315(2)            |
| S(1)  | 4144(1)   | 583(2)   | 619(1)  | 359(8)            |
| S(2)  | 3230(1)   | -1308(2) | 1329(1) | 355(8)            |
| S(3)  | 3128(1)   | 1465(2)  | 1680(1) | 382(8)            |
| P(1)  | 4726(1)   | -0015(2) | 1301(1) | 310(8)            |
| P(2)  | 3848(1)   | -1041(2) | 2053(1) | 301(8)            |
| P(3)  | 4025(1)   | 1287(2)  | 2103(1) | 315(8)            |
| C(1)  | 2544(4)   | 1601(6)  | 228(4)  | 49(4)             |
| C(2)  | 2804(4)   | 835(8)   | -137(3) | 42(4)             |
| C(3)  | 2646(3)   | -241(7)  | -66(3)  | 38(3)             |
| C(4)  | 2222(3)   | -537(6)  | 348(3)  | 36(3)             |
| C(5)  | 1940(4)   | 224(7)   | 702(3)  | 39(3)             |
| C(6)  | 2123(4)   | 1292(7)  | 630(3)  | 39(3)             |
| C(7)  | 3246(4)   | 1164(7)  | -585(3) | 72(4)             |
| C(8)  | 827(3)    | -425(7)  | 771(3)  | 80(4)             |
| C(9)  | 1363(4)   | 671(8)   | 1577(4) | 96(5)             |
| C(10) | 1469(4)   | -132(7)  | 1109(4) | 55(4)             |
| C(11) | 4371(3)   | 43(5)    | 1973(3) | 27(3)             |
| C(12) | 5486(3)   | 711(6)   | 1358(3) | 33(3)             |
| C(18) | 4969(4)   | -1354(6) | 1129(3) | 30(3)             |
| C(24) | 4326(4)   | -2226(6) | 2225(3) | 28(3)             |
| C(30) | 3385(4)   | -905(5)  | 2671(3) | 33(3)             |
| C(36) | 3972(4)   | 1440(6)  | 2876(3) | 32(3)             |
| C(42) | 4538(4)   | 2359(6)  | 1896(4) | 31(3)             |

<sup>a</sup>The atomic coordinates of the phenyl groups—excepting those of the *ipso* carbons—and those of the anions have been omitted.

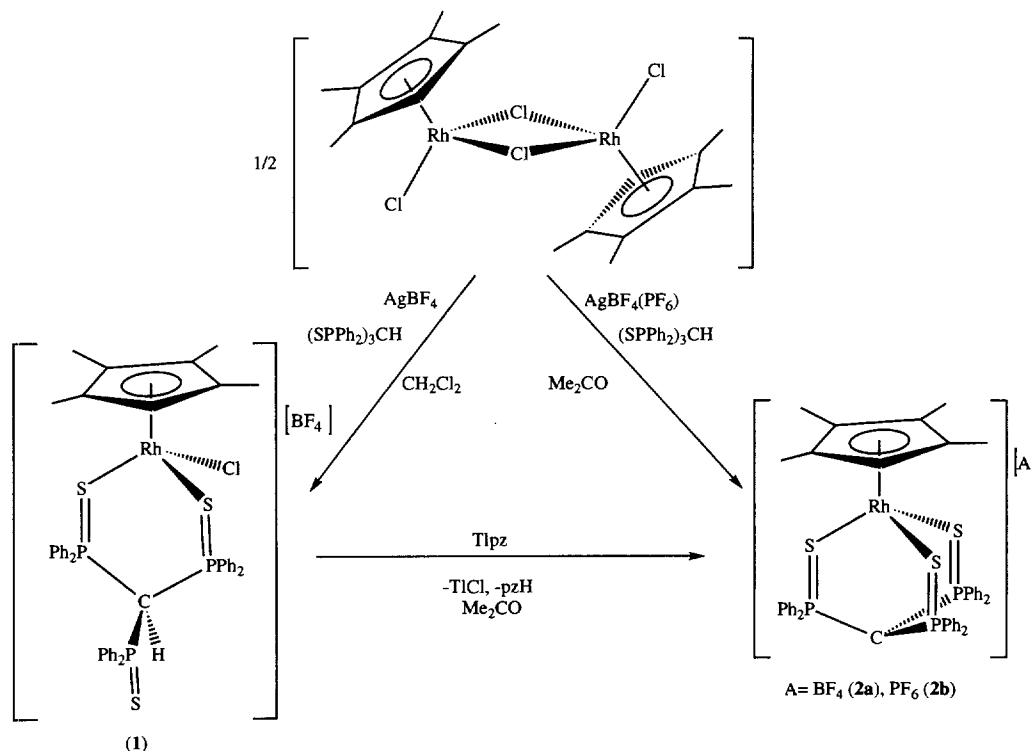
<sup>b</sup> $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

ture; unfortunately it converges to an intermediate value, 0.450(6), indicating likely the presence of a mixture of crystals of both polarities [33]. Atomic scattering factors, corrected for anomalous dispersion, were taken from Ref. [34]. Final atomic coordinates are given in Tables 1 and 2.

### 3. Results and discussion

#### 3.1. Synthesis and characterization of the new complexes

In dichloromethane solution, the binuclear complex  $\{[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2]_2\}$  reacted with silver tetrafluoroborate, in a 1:2 molar ratio, to form silver chloride and, most probably, the solvate complex  $\{[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}(\text{solvent})_2]^+\}$ , which further reacted with  $(\text{SPPH}_2)_3\text{CH}$  to give the cationic compound  $\{[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}(\eta^2\text{-}(\text{SPPH}_2)_2\text{CH}(\text{SPPH}_2)\text{-S,S'})]\text{BF}_4$  (**1**). The  $^1\text{H}$  NMR spectrum of complex **1** exhibited a singlet signal at  $\delta$  1.59 ppm, attributed to the  $\text{C}_5\text{Me}_5$  group, together with two multiplets, in the 7.0–8.0 ppm region, corresponding to the phenyl protons of the sulphur ligand. At room temperature, the methine proton was not observed, but at  $-60^\circ\text{C}$ , it appeared as a broad singlet at 6.35 ppm. While, at room temperature, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **1** only showed a broad resonance centred at 44.4 ppm, at  $-60^\circ\text{C}$ , it exhibited



Scheme 1.

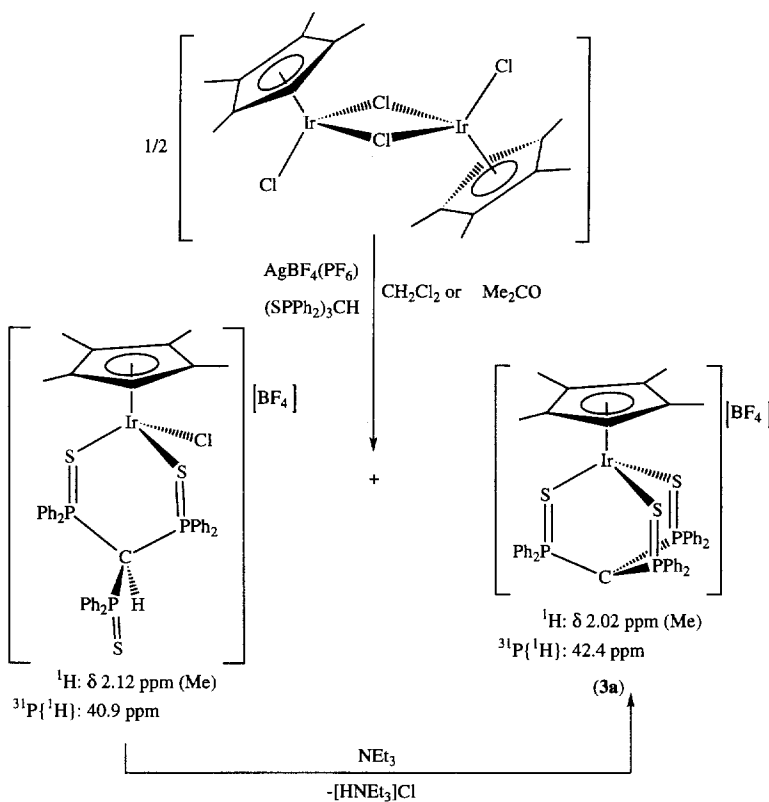
two broad singlets at 43.6 and 44.6 ppm, in an intensity ratio of 2:1. Although the low-temperature limiting spectrum was not achieved, the NMR data can be accounted for by assuming that a fluxional-exchange kinetic process, that averaged the three arms of the sulphur ligand, was operating. Below  $-60^{\circ}\text{C}$  and, most probably, also in the solid state, the sulphur ligand would be  $\eta^2$ -coordinated to the rhodium through two of its sulphur atoms, the third one remaining free.

Complex **1** could be deprotonated by thallium(I) pyrazolate, in acetone solution, to afford insoluble thallium(I) chloride, pyrazole and the new cationic complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\eta^3\text{-(SPPH}_2)_3\text{C-S,S',S''})]\text{BF}_4$  (**2a**). Complex **2a**, or the related hexafluorophosphate salt  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\eta^3\text{-(SPPH}_2)_3\text{C-S,S',S''})]\text{PF}_6$  (**2b**), can also be prepared directly from the binuclear complex  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{RhCl}_2]_2$ , the corresponding silver salt ( $\text{AgA}$ ,  $\text{A} = \text{BF}_4^-, \text{PF}_6^-$ ), and  $(\text{SPPH}_2)_3\text{CH}$  in acetone ( $\text{BF}_4^-$ ) or dichloromethane/acetone ( $\text{PF}_6^-$ ) solvents (Scheme 1). At room temperature, the  $^1\text{H}$  NMR spectrum of complex **2a** exhibited a singlet resonance at 2.00 ppm attributed to the  $\text{C}_5\text{Me}_5$  group and the proton decoupled  $^{31}\text{P}$  spectrum consisted of a doublet centred at 44.4 ppm with a coupling constant,  $^2J(\text{RhP})$ , of 3.6 Hz. At  $-60^{\circ}\text{C}$ , the  $^{31}\text{P}\{^1\text{H}\}$  spectrum remained essentially unchanged, indicating that the  $\text{S,S',S''}$ -tridentate coordination was present in all the range of temperature investigated.

The homologous dimeric iridium(III) complex  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{IrCl}_2]_2$  reacted with  $\text{AgA}$  ( $\text{A} = \text{BF}_4^-, \text{PF}_6^-$ ),

and  $(\text{SPPH}_2)_3\text{CH}$ , in both dichloromethane or acetone solutions, to afford mixtures of two iridium complexes containing the sulfur ligand  $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}(\eta^2\text{-(SPPH}_2)_2\text{CH(SPPH}_2)_2\text{-S,S'})]\text{A}$  and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^3\text{-(SPPH}_2)_3\text{C-S,S',S''})]\text{A}$  ( $\text{A} = \text{BF}_4^-$  (**3a**),  $\text{PF}_6^-$  (**3b**)) (Scheme 2). These results confirmed that, as expected, the acidity of the methine proton was enhanced by coordination. Consequently, complexes **3** were the result of a spontaneously partial loss of hydrogen chloride, which promoted a change in the hapticity of the sulfur ligand from  $\eta^2$  to  $\eta^3$ . Obviously, the addition of  $\text{Et}_3\text{N}$  to a solution of the mixture caused the total deprotonation of the coordinated chelate ligand affording pure complexes **3**.

All cationic complexes were isolated as stable microcrystalline solids and behaved as 1:1 electrolytes in acetone solution. In all cases their infrared spectra in KBr pellets showed the presence of the uncoordinated anion ( $\text{BF}_4^-$ : ca. 1050, 510  $\text{cm}^{-1}$ ;  $\text{PF}_6^-$ : ca. 840, 560  $\text{cm}^{-1}$ ) together with the absorption band corresponding to the coordinated  $\text{P}=\text{S}$  groups. As expected, the  $\nu(\text{PS})$  stretchings were shifted to lower frequencies [ $\nu(\text{PS}) = 548\text{--}556 \text{ cm}^{-1}$ ] relative to that of the free neutral ligand [ $\nu(\text{PS}) = 574 \text{ cm}^{-1}$ ], but appeared at similar wavenumbers to those of the lithium or tetramethylammonium salts  $\text{Q}[(\text{SPPH}_2)_3\text{C}]$  [ $\nu(\text{PS}) = 546$  and 550  $\text{cm}^{-1}$ , respectively] [19]. The mass spectra of complexes **2b** and **3a** ( $\text{FAB}^+$  mode) showed an envelope of peaks at  $m/z$  901 and 991, respectively, with isotopic



distributions that matched those calculated for the proposed cationic formulations. The mass spectrum of compound **1** was identical to that of compound **2b**, as expected from the easy loss of hydrogen chloride that this type of compounds undergoes.

On the other hand, the reaction of the binuclear ruthenium(II) complexes  $[(\eta^6\text{-arene})\text{RuCl}_2]_2$  with  $(\text{SPPPh}_2)_3\text{CH}$ , in dichloromethane or acetone, in the presence of silver hexafluorophosphate or tetrafluoroborate or sodium tetraphenylborate, only yielded the cationic complexes  $[(\eta^6\text{-arene})\text{Ru}(\eta^3\text{-}(\text{SPPPh}_2)_3\text{C-S,S',S''})\text{A}]$  [arene =  $\text{C}_6\text{Me}_6$ ,  $\text{A} = \text{BF}_4^-$ , arene = *p*- $\text{MeC}_6\text{H}_4\text{Pr}^i$  (*p*-cymene),  $\text{A} = \text{BPh}_4^-$  (**4a**),  $\text{PF}_6^-$  (**4b**)] in which the  $(\text{SPPPh}_2)_3\text{C}$  group was acting as an anionic tridentate ligand. At room temperature, the  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of the  $\text{C}_6\text{Me}_6$  complex exhibited singlet resonances at 2.00 and 44.9 ppm, respectively. At  $-60^\circ\text{C}$ , the  $^{31}\text{P}\{^1\text{H}\}$  NMR resonance remained essentially unchanged. This complex was isolated as a red microcrystalline solid but all attempts to obtain analytical pure samples were unsuccessful due to the presence of variable amounts of the used solvent, as assayed by  $^1\text{H}$  NMR spectroscopy. However, analytically pure samples of the *p*-cymene complexes **4a** and **4b** were isolated and fully characterized. Their  $^1\text{H}$  NMR spectra showed the expected resonances for the coordinated *p*-cymene group along with the multiplets for the phenyl protons. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra, at room temperature, consisted of a singlet resonance at 43.65 ppm for the three equivalent phosphorus atoms.

It is interesting to point out the different behaviour of the  $(\text{SPPPh}_2)_3\text{CH}$  ligand towards the in situ generated

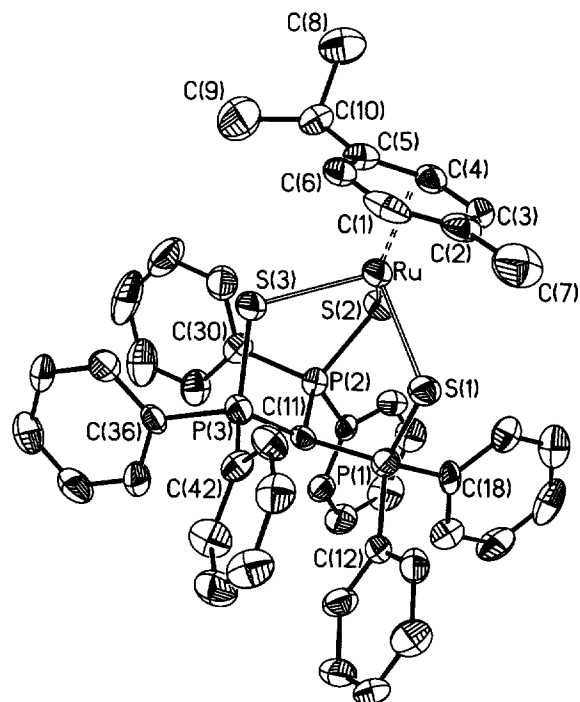


Fig. 2. Molecular drawing of the metallic complex of **4a** with the labelling scheme used.

$[(\text{ring})\text{MCl}(\text{solvent})_2]^+$  cations. When (ring)M was  $(\text{C}_5\text{Me}_5)\text{Rh}$ , depending on the polarity of the solvent, the deprotonated complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}\{\eta^3\text{-}(\text{SPPPh}_2)_3\text{C-S,S',S''}\}]^+$ , with the  $(\text{SPPPh}_2)_3\text{C}^-$  anion acting as  $\eta^3$ -ligand, or the cation  $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}\{\eta^2\text{-}(\text{SPPPh}_2)_2\text{CH}(\text{SPPPh}_2)\text{-S,S'}\}]^+$ , in which the  $(\text{SPPPh}_2)_3\text{CH}$  ligand is  $\eta^2$  coordinated, were formed. Thus, while in dichloromethane we obtained complex **1**, in acetone, the isolated complexes were **2a** or **2b**. When (ring)M was  $(\text{C}_5\text{Me}_5)\text{Ir}$ , in both dichloromethane or acetone solvents, mixtures of the corresponding  $\eta^3$ - and  $\eta^2$ -coordinated ligand complexes **3** and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}_2\{\eta^2\text{-}(\text{SPPPh}_2)_2\text{CH}(\text{SPPPh}_2)\text{-S,S'}\}]^+$ , respectively, were obtained. Finally, when (ring)M was (arene)Ru, only complexes with the deprotonated  $\eta^3$ -coordinated  $(\text{SPPPh}_2)_3\text{C}$  ligand were obtained.

### 3.2. X-ray crystal structures of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}\{\eta^3\text{-}(\text{SPPPh}_2)_3\text{C-S,S',S''}\}]\text{BF}_4$ (**3a**) and $[(\eta^6\text{-p-MeC}_6\text{H}_4\text{Pr}^i)\text{Ru}\{\eta^3\text{-}(\text{SPPPh}_2)_3\text{C-S,S',S''}\}]\text{BPh}_4$ (**4a**)

Although the spectroscopic data observed in solution, fundamentally those of the  $\nu(\text{P}=\text{S})$  IR bands and the  $^{31}\text{P}\{^1\text{H}\}$  NMR signals, suggest a tripodal tridentate coordination of the  $(\text{SPPPh}_2)_3\text{C}^-$  ligand for both iridium (**3a**) and ruthenium (**4a**) complexes, two analyses by X-ray diffraction methods were carried out to firmly establish their molecular structures and to obtain additional information on molecular parameters. Figs. 1 and 2 represent

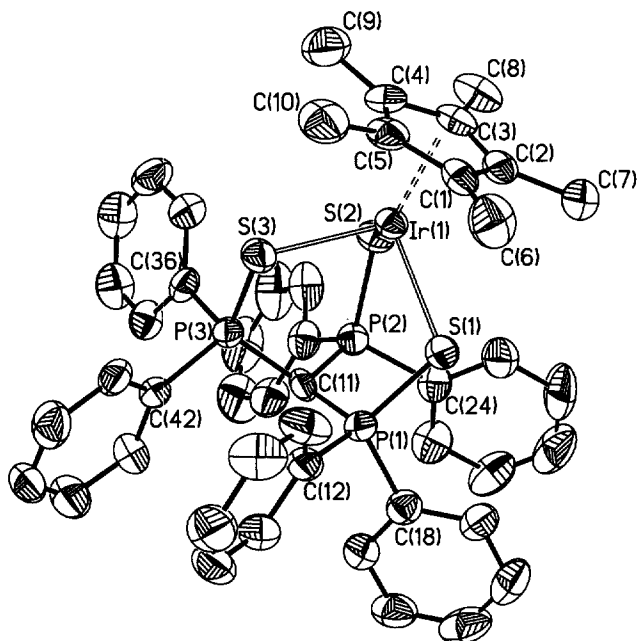


Fig. 1. Molecular structure of the complex cation in **3a** with atom-numbering scheme. Hydrogen atoms are omitted for clarity.

Table 3

Selected bond distances and angles for complexes  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^3\text{-}(\text{SPPPh}_2)_3\text{C-S,S',S''})]\text{BF}_4$  (**3a**)<sup>a</sup> and  $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^1)\text{Ru}(\eta^3\text{-}(\text{SPPPh}_2)_3\text{C-S,S',S''})]\text{BPh}_4$  (**4a**)

|                           | <b>3a</b> | <b>4a</b> | <b>4a</b> |
|---------------------------|-----------|-----------|-----------|
| Ir/Ru–S(1)                | 2.44(3)   | 2.428(2)  | 2.443(2)  |
| Ir/Ru–S(2)                | 2.409(3)  | 2.433(2)  | 2.451(2)  |
| Ir/Ru–S(3)                | 2.409(2)  | 2.429(3)  | 2.438(2)  |
| Ir/Ru–C(1)                | 2.163(9)  | 2.163(11) | 2.201(8)  |
| Ir/Ru–C(2)                | 2.161(9)  | 2.246(9)  | 2.248(8)  |
| Ir/Ru–C(3)                | 2.183(9)  | 2.159(9)  | 2.214(7)  |
| Ir/Ru–C(4)                | 2.169(9)  | 2.159(10) | 2.187(7)  |
| Ir/Ru–C(5)                | 2.173(8)  | 2.175(12) | 2.236(7)  |
| Ir/Ru–C(6)                | –         | –         | 2.189(8)  |
| Ir/Ru–G <sup>b</sup>      | 1.799(9)  | 1.793(11) | 1.705(7)  |
| S(1)–P(1)                 | 2.034(3)  | 2.025(3)  | 2.031(3)  |
| S(2)–P(2)                 | 2.024(3)  | 2.027(3)  | 2.031(3)  |
| S(3)–P(3)                 | 2.041(3)  | 2.036(3)  | 2.030(3)  |
| P(1)–C(11)                | 1.759(10) | 1.747(9)  | 1.787(7)  |
| P(2)–C(11)                | 1.785(9)  | 1.755(9)  | 1.765(6)  |
| P(3)–C(11)                | 1.755(9)  | 1.778(9)  | 1.758(6)  |
| P(1)–C(12)                | 1.813(11) | 1.811(9)  | 1.819(7)  |
| P(1)–C(18)                | 1.814(11) | 1.804(9)  | 1.811(7)  |
| P(2)–C(24)                | 1.803(9)  | 1.842(9)  | 1.813(8)  |
| P(2)–C(30)                | 1.810(11) | 1.811(10) | 1.809(9)  |
| P(3)–C(36)                | 1.832(9)  | 1.828(9)  | 1.810(7)  |
| P(3)–C(42)                | 1.809(9)  | 1.809(9)  | 1.812(8)  |
| C(1)–C(2)                 | 1.403(14) | 1.46(14)  | 1.421(12) |
| C(1)–C(5)                 | 1.408(14) | 1.45(2)   | –         |
| C(1)–C(6)                 | 1.49(2)   | 1.47(2)   | 1.394(12) |
| C(2)–C(3)                 | 1.420(14) | 1.420(2)  | 1.404(13) |
| C(2)–C(7)                 | 1.543(14) | 1.53(2)   | 1.509(11) |
| C(3)–C(4)                 | 1.450(13) | 1.38(2)   | 1.416(10) |
| C(3)–C(8)                 | 1.49(2)   | 1.53(2)   | –         |
| C(4)–C(5)                 | 1.45(2)   | 1.40(2)   | 1.422(11) |
| C(4)–C(9)                 | 1.50(2)   | 1.52(2)   | –         |
| C(5)–C(6)                 | –         | –         | 1.408(12) |
| C(5)–C(10)                | 1.491(14) | 1.147(2)  | 1.494(11) |
| C(8)–C(10)                | –         | –         | 1.521(10) |
| C(9)–C(10)                | –         | –         | 1.510(12) |
| S(1)–Ir/Ru–S(2)           | 96.0(1)   | 95.1(1)   | 92.9(1)   |
| S(1)–Ir/Ru–S(3)           | 95.5(1)   | 96.8(1)   | 94.1(1)   |
| S(1)–Ir/Ru–G <sup>b</sup> | 120.7(3)  | 121.5(4)  | 123.9(3)  |
| S(2)–Ir/Ru–S(3)           | 94.5(1)   | 94.5(1)   | 94.4(1)   |
| S(2)–Ir/Ru–G <sup>b</sup> | 122.2(3)  | 120.1(4)  | 122.5(3)  |
| S(3)–Ir/Ru–G <sup>b</sup> | 121.3(3)  | 122.3(4)  | 121.4(3)  |
| Ir/Ru–S(1)–P(1)           | 108.4(1)  | 107.2(1)  | 109.5(1)  |
| Ir/Ru–S(2)–P(2)           | 108.2(2)  | 107.4(1)  | 109.5(1)  |
| Ir/Ru–S(3)–P(3)           | 107.9(1)  | 108.0(2)  | 110.1(1)  |
| S(1)–P(1)–C(11)           | 112.0(3)  | 112.0(3)  | 113.1(2)  |
| S(1)–P(1)–C(12)           | 108.7(3)  | 108.9(3)  | 108.5(3)  |
| S(1)–P(1)–C(18)           | 110.4(3)  | 108.9(3)  | 109.3(2)  |
| C(11)–P(1)–C(12)          | 111.9(4)  | 112.1(4)  | 110.5(3)  |
| C(11)–P(1)–C(18)          | 108.2(5)  | 110.3(4)  | 112.2(3)  |
| C(12)–P(1)–C(18)          | 105.4(5)  | 104.4(4)  | 102.8(3)  |
| S(2)–P(2)–C(11)           | 112.1(3)  | 112.2(3)  | 112.8(2)  |
| S(2)–P(2)–C(24)           | 108.9(4)  | 110.1(3)  | 109.5(2)  |
| S(2)–P(2)–C(30)           | 109.2(4)  | 109.4(4)  | 108.8(3)  |
| C(11)–P(2)–C(24)          | 112.8(5)  | 110.8(4)  | 108.9(3)  |
| C(11)–P(2)–C(30)          | 110.1(5)  | 108.4(4)  | 113.1(3)  |
| C(24)–P(2)–C(30)          | 103.4(4)  | 105.7(4)  | 103.2(3)  |
| S(3)–P(3)–C(11)           | 112.9(3)  | 111.3(3)  | 112.8(2)  |
| S(3)–P(3)–C(36)           | 109.6(3)  | 108.8(3)  | 108.6(3)  |
| S(3)–P(3)–C(42)           | 107.8(3)  | 110.8(3)  | 109.2(3)  |

Table 3 (continued)

|                  | <b>3a</b> | <b>3a</b> | <b>4a</b> |
|------------------|-----------|-----------|-----------|
| C(11)–P(3)–C(36) | 111.6(4)  | 113.9(4)  | 109.2(3)  |
| C(11)–P(3)–C(42) | 110.0(4)  | 108.5(4)  | 110.6(3)  |
| C(36)–P(3)–C(42) | 104.6(4)  | 103.3(4)  | 106.1(4)  |
| P(1)–C(11)–P(2)  | 113.2(4)  | 114.4(5)  | 111.9(3)  |
| P(1)–C(11)–P(3)  | 114.2(5)  | 114.3(5)  | 113.4(3)  |
| P(2)–C(11)–P(3)  | 112.6(5)  | 112.8(5)  | 113.6(4)  |

<sup>a</sup>The first two figures for each parameter correspond to the values observed for the two crystallographically independent molecules in **3a**.

<sup>b</sup>G represents the ring centroids of the cyclic pentamethylcyclopentadienyl (**3a**) or *p*-cymene (**4a**) ligands.

molecular drawings for the cations of the complexes **3a** and **4a**, respectively. Table 3 collects the selected bond distances and angles for both structures.

The molecular structures for both cations are rather similar. In both cases the metal centres display a *pseudo*-octahedral coordination geometry with an anionic  $(\text{SPPPh}_2)_3\text{C}^-$  ligand bonded through the three sulphur atoms in a tripodal tridentate fashion, and a cyclic  $\eta^5\text{-C}_5\text{Me}_5$  ligand in **3a** or a *p*-cymene arene in **4a** completing the metal coordination sphere (Figs. 1 and 2). Likely the larger and more symmetric steric requirements of the  $\eta^5\text{-C}_5\text{Me}_5$  group in **3a**, compared to those of the *p*-cymene in **4a**, affects the coordination of the tridentate S-donor ligand originating smaller S–M–S angles in **4a** (av. 93.8(5)°) than those observed in **3a** (av. 95.3(4) and 95.5(7)°; the two mean values reported along discussion for **3a** refer to the two crystallographic independent molecules found in the crystal structure).

All the Ir–S bond distances in **3a** are rather similar, and are within the range 2.409(3)–2.442(3) Å. These distances are significantly longer than those observed in the closely related neutral iridium(I) complexes  $[\text{Ir}(\eta^2\text{-}(\text{SPPPh}_2)_2\text{C}(\text{SPPPh}_2)\text{-S,S}')(\text{COD})]$  (2.382(2) and 2.326(3) Å) [21] or  $[\text{Ir}(\eta^2\text{-}(\text{SPPPh}_2)_2\text{C}(\text{SPPPh}_2)\text{-S,S}')(\text{CO})_2]$  (2.348(8) and 2.370(7) Å) [18] where the  $(\text{SPPPh}_2)_3\text{C}$  methanide ligand is  $\eta^2\text{-S,S'}$ -bonded to the iridium centres, or in sulphido-iridium(III) complexes containing the  $(\text{C}_5\text{Me}_5)\text{IrS}_3$  moiety as in the cubane-like cluster  $\{(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}\}_4(\mu_3\text{-S})_4$  [35,36] (mean 2.373(4) Å) or in the dinuclear  $\{(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}\}_2(\mu_2\text{-S}_4)_2$  [37] (range 2.313–2.404(2) Å). These rather long Ir–S bond distances probably suggest the interaction established between the metal and the S atoms to be rather weak.

In the case of the structurally analogous ruthenium complex **4a**, the Ru–S bond lengths (range 2.438–2.451(2) Å) compare well with those found in the related compounds  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-}(\text{SPPPh}_2)_2\text{CH-C,S,S}')]\text{ClO}_4$  (av. 2.443(1) Å) [14] and  $[(\eta^6\text{-MeC}_6\text{H}_4\text{Pr}^1)\text{Ru}(\eta^3\text{-}(\text{SPPPh}_2)_2\text{CMe-C,S,S}')]\text{BPh}_4$  [av. 2.435(4) Å] [17], but are also in the upper range of



Ru–S bond distances observed in *pseudo*-octahedral *p*-cymene–ruthenium(II) complexes (2.263–2.472 Å) [38].

All the Ir–C distances in **3a** (range 2.146(9)–2.175(12) Å, including both independent molecules) are statistically equivalent, according to the symmetric coordination of the methanide ligand located in the opposite part of the metal coordination sphere. The Ir–centroid(C<sub>5</sub>Me<sub>5</sub>) distances, 1.799(9) and 1.793(11) Å, exhibit normal values for this type of interaction [16,39–41]. On the other hand, the refined Ru–C distances present two different groups of values: two long (C(2) and C(5), 2.248(8) and 2.236(7) Å) and four short (range 2.187–2.214(7) Å). These data indicate a slight deformation of the ideally planar *p*-cymene ring towards a boat conformation with the tertiary substituted carbon atoms out of the plane. However, these Ru–C distance values are comparable to those reported in other *p*-cymene–ruthenium(II) complexes [17,42,43]. Fig. 3 represents a schematic view of the metal coordination core showing the relative orientation of the tridentate methanide ligand respect to the η<sup>5</sup>- or η<sup>6</sup>-coordinated carbocyclic groups.

The most conspicuous feature of the cationic complexes concerns the coordination of the tridentate anionic (SPPPh<sub>2</sub>)<sub>3</sub>C<sup>-</sup> ligand. This ligand exhibits a parallel behaviour in both cations, **3a** and **4a**; in spite of the different metal centre, the structural parameters within the S-donor ligand are statistically identical in both structures (see Table 3). As observed in the two previously reported structures containing a tridentate-S,S',S'' methanide ligand, [Ag(PBu<sub>3</sub>)<sub>3</sub>(η<sup>3</sup>-(SPPPh<sub>2</sub>)<sub>3</sub>C-S,S',S'')] [24] and [HgCl(η<sup>3</sup>-(SPPPh<sub>2</sub>)<sub>3</sub>C-S,S',S'')] [44], the coordination of this ligand causes a lengthening of the P–S distance from 1.942(5) Å in the neutral (SPPPh<sub>2</sub>)<sub>3</sub>CH species [45], and 1.976 Å in the anionic (SPPPh<sub>2</sub>)<sub>3</sub>C<sup>-</sup> group [46], to mean values of 2.033(5) and 2.029(3) Å in **3a** and 2.031(2) in **4a**. This lengthening is probably due to a reduction of the available electron

density at the S atom upon coordination as it has also been reported when phosphine chalcogenides undergo complexation [18,24,44]. According to this proposal, the non-coordinated P–S bond distances in metal complexes containing the bidentate η<sup>2</sup>-(SPPPh<sub>2</sub>)<sub>2</sub>C(SPPPh<sub>2</sub>-S,S') ligand maintain values (1.964(5) in [PtCl(PEt<sub>3</sub>)<sub>3</sub>(η<sup>2</sup>-(SPPPh<sub>2</sub>)<sub>2</sub>C(SPPPh<sub>2</sub>-S,S'))] [20] and 1.969(10) in [Ir(η<sup>2</sup>-(SPPPh<sub>2</sub>)<sub>2</sub>C(SPPPh<sub>2</sub>-S,S')(CO)<sub>2</sub>] [18], for instance) close to those observed in the free neutral ligand (SPPPh<sub>2</sub>)<sub>3</sub>CH (1.942(5)) Å [45]. Simultaneously to the P–S bond elongation, the deprotonation of the methanide carbon significantly shortens the P–C(11) separation from 1.881(7) in (SPPPh<sub>2</sub>)<sub>3</sub>CH to 1.767(10) and 1.760(9) Å in **3a** and 1.768(8) in **4a**. The comparison between the latter values and those of the exocyclic P–C(Ph) bonds (av. 1.819(4) and 1.818(6) Å in **3a**, and 1.813(3) Å in **4a**), clearly demonstrates the existence of a partial double bond between the bridgehead carbon and the phosphorous atoms. Probably the participation of some mesomeric stabilization also strengthens the P–C(11) bonds, as it has been previously suggested for the anionic (SPPPh<sub>2</sub>)<sub>3</sub>C<sup>-</sup> species [46] or in the previously mentioned Ag(I) or Hg(II) complexes containing the η<sup>3</sup>-(SPPPh<sub>2</sub>)<sub>3</sub>C<sup>-</sup> anion [24,44].

Quite interesting to note is the geometry observed in both cations around the tricoordinated bridgehead carbon, C(11). It markedly deviates from the ideal trigonal planar arrangement described for the uncomplexed anion (SPPPh<sub>2</sub>)<sub>3</sub>C<sup>-</sup> (av. P–C–P angle 119.9°) showing P–C–P angular values closer to those of standard tetrahedral carbons (av. 113.3(4) and 113.8(5)° in **3a**, and 112.9(5)° in **4a**). Analogous but smaller deviations from planarity have also been observed in the related [Ag(PBu<sub>3</sub>)<sub>3</sub>(η<sup>3</sup>-(SPPPh<sub>2</sub>)<sub>3</sub>C-S,S',S'')] (av. 115.9(3)°) and [HgCl(η<sup>3</sup>-(SPPPh<sub>2</sub>)<sub>3</sub>C-S,S',S'')] (av. 116.4(4)°) complexes; however the values in these cases approximate the ideal trigonal situation. Most probably the tetrahedral metal coordination of these complexes, allowing greater S–M–S angles (100.4(11)° in Ag(I), and

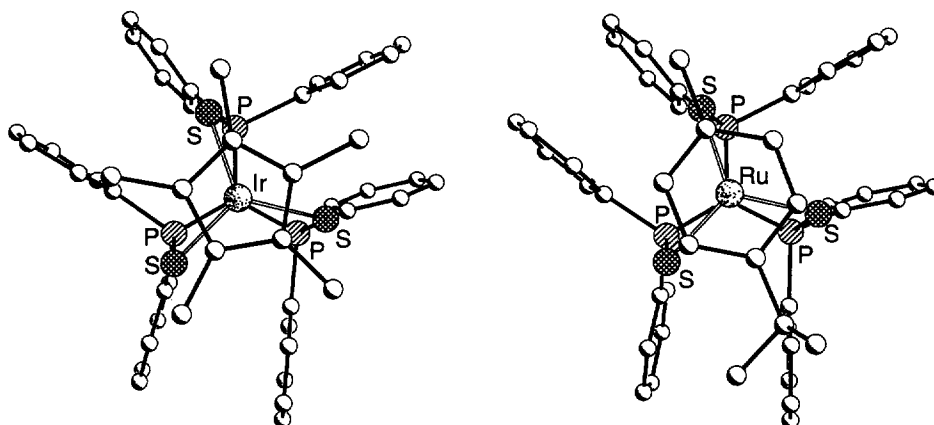


Fig. 3. Schematic representation of the metallic complexes **3a** and **4a** viewed along the M–C(methanide) direction.

102(4)° in Hg(II) complexes) produces appreciable conformational changes in the three six-membered chelated rings, affecting also significantly to the M–S–P and S–P–C angles (av. 97.1(4) and 115.9(2)° in the Ag(I) cation, and av. 96.2(8) and 114.9(2)° in the related Hg(II) compound). In our *pseudo*-octahedral complexes, **3a** and **4a**, these M–S–P and S–P–C angles exhibit less strained values, which are very close to those expected for tetrahedral geometries (M–S–P: av. 108.2(2) and 107.4(2)° in **3a**, and 109.7(2) in **4a**; S–P–C(11): av. 112.3(3) and 111.8(3) in **3a**, and 112.9(1) in **4a**).

### 3.3. Redox behaviour of the complexes

Complexes **1–4** were studied by cyclic voltammetry in acetonitrile. The cyclic voltammograms of complex **1a** (Fig. 4A) showed an electrochemically quasi-reversible two-electron reduction process, metal-localized ( $E_{pc} = -1.15$  V,  $E_{pa} = -1.03$  V vs. SCE), followed by an irreversible reduction at  $-1.94$  V. On scanning from 0 to  $+1.6$  V, a quasi-reversible oxidation occurred ( $E_{pc} = 1.55$  V and  $E_{pa} = 1.45$  V, SCE). The two latter

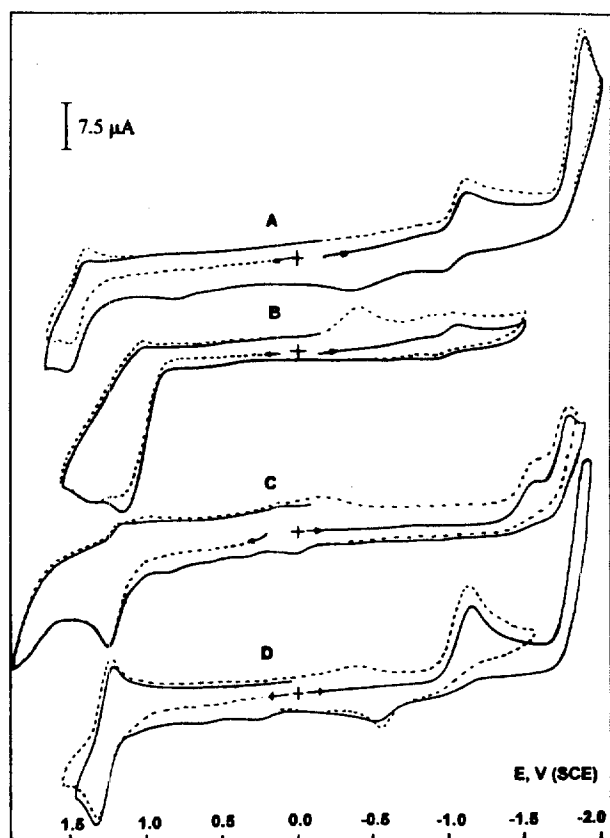
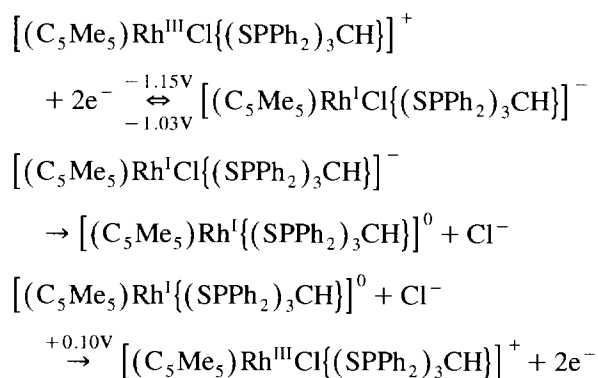


Fig. 4. Cyclic voltammograms of 1 mM solutions of complexes in acetonitrile using 0.2 M tetraethylammonium perchlorate (TEAP) as supporting electrolyte. (A) **1**, (B) **2a**, (C) **3a** and (D) **4a**. The scan rate was  $0.2 \text{ V s}^{-1}$  in all cases. The working electrode was a platinum disc.

electron-transfer processes were associated as most likely to the coordinated chalcogenide ligand since the free ligand showed two irreversible waves at  $E_{pc} = -1.80$  V (reduction) and at  $E_{pa} = 1.40$  V (oxidation). Controlled potential electrolysis on a graphite pyrolytic electrode at  $-1.35$  V consumed two electrons per mol of complex. The final product of this electrolysis contained free chloride which resulted in a positive shift (ca. 0.10 V) for the wave corresponding to the re-oxidation of the metal from Rh(I) to Rh(III). In the cyclic voltammograms at slow scan rates ( $10 \text{ mV/s}$ ), the presence of free chloride (oxidation at 1.00 V approximately) was not observed when the experiment was carried out to negative potential scan, suggesting that the chloride liberation was a slow process.

Furthermore, the ipa/ipc ratio for the metal-localized two-electron reduction process was  $< 1$ , confirming that the reduction of the metal was coupled with a chemical reaction [47]:



The cyclic voltammograms of complex **2a** (Fig. 4B) exhibited a quasi-reversible Rh(III)–Rh(I) reduction ( $E_{pc} = -1.08$  V;  $E_{pa} = -0.94$  V, SCE). On scanning from 0 to  $+1.6$  V, a very broad oxidation peak at 1.14 V with two reductions at  $E_{pc} = 1.06$  V and  $E_{pc} = -0.4$  V coupled to it were observed. These data suggested that the deprotonated chalcogenide ligand in compound **2a** was more easily oxidized than its protonated analogue present in complex **1**. Moreover, the value of the intensity current associated to this oxidation indicated that a more complex processes was occurring at this potential. Controlled potential electrolysis at 1.34 V showed the presence of free protons (the signal at  $-0.4$  V increased when  $HClO_{4(aq)}$  was added) indicating that, at this potential, both pentamethylcyclopentadienyl [48] and chalcogenide coordinated ligands were oxidized.

Cyclic voltammograms of complex **3a** showed an irreversible metal-localized two-electron reduction Ir(III)–Ir(I) at  $-1.62$  V (Fig. 4C). The quasi-reversible oxidation of the chalcogenide ligand occurred at  $E_{pa} = 1.30$  V and  $E_{pc} = 1.22$  V.

The cyclic voltammograms of the Ru(II) complex **4a** (Fig. 4D) exhibited two reduction peaks at  $-1.20$  V (with one oxidation peak at  $-0.58$  V coupled to it) and

–1.98 V. The first reduction process involved one electron per mol of compound and produced an unstable Ru(I) species, which further underwent a chemical reaction. On scanning toward positive voltages, a quasi-reversible oxidation peak occurred at 1.37 V to give a Ru(III) complex which, in turn, was reduced at 1.26 V. The controlled potential electrolysis at 1.57 V indicated that one equivalent of charge was transferred in this process. The resulting solution was reduced at –0.36 V suggesting that the electrolytical process was followed by some structural changes.

#### 4. Supplementary material available

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

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